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Arsenic Removal for Small Drinking Water Treatment Systems: A Multimedia CD-ROM for Drinking Water Professionals

Greg A. Harrison
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To the Graduate Council:

I am submitting herewith a thesis written by Greg A. Harrison entitled "Arsenic Removal for Small Drinking Water Treatment Systems: A Multimedia CD-ROM for Drinking Water Professionals." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

Dr. R. Bruce Robinson, Major Professor

We have read this thesis and recommend its acceptance:

Dr. Wayne T. Davis, Dr. Bruce A. Tschantz

Accepted for the Council:
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Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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ARSENIC REMOVAL FOR SMALL DRINKING WATER TREATMENT SYSTEMS: A Multimedia CD-ROM for Drinking Water Professionals

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Greg A. Harrison
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DEDICATION

This thesis is dedicated to my parents Mr. Sherman Harrison and Mrs. Linda Harrison who gave me encouragement to pursue my dreams and invaluable support to further my education at The University of Tennessee.

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ABSTRACT

This thesis, in conjunction with the accompanying CD-ROM, are intended to be used by small public water system operators, owners, regulators, and engineers as an educational tool for future compliance with a lowered Arsenic Maximum Contaminant Level (MCL). The CD-ROM is the third in a series of water treatment technology CDs that were created by a collaboration of Dr. R. Bruce Robinson, the University of Tennessee, and Dr. M. Robin Collins, the Water Treatment Technology Center, the University of New Hampshire. The CD-ROM includes multimedia tools such as video and photos, which will aid in the understanding of the included descriptive text of processes and operations involved in the removal of arsenic. The thesis includes a literature review on arsenic removal from drinking water systems and a discussion on the process and methodology that was undertaken to create the CD-ROM.

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CHAPTER 1

INTRODUCTION

1.1 Background

Arsenic removal from drinking water systems in the United States has become a very important topic recently with concerns about the current maximum contaminant level (MCL) in the U.S. not being adequate for the protection of human health. In June of 2000, the U.S. EPA proposed dropping the MCL for arsenic from 50 μg/L to 5 μg/L, thus raising the concern of how utilities would meet the new standard. In January of 2001, EPA issued a final rule setting the new MCL at 10 μg/L, a five-fold decrease from the current MCL. As of this writing, the final rule has been rescinded by EPA pending further study. Arsenic was regulated in the past because it was a Class I carcinogen and was thought to cause skin cancer in humans. Recent epidemiological studies in Taiwan have indicated that arsenic in drinking water may also increase risks of bladder and lung cancers in humans as well (U.S. EPA, 1998). The EPA estimates that 5.3% of ground water community water systems (CWSs) and 0.80% of surface water CWSs have average finished water arsenic levels above 10 μg/L (U.S. EPA, 2001b). The EPA also estimates that under a final MCL of 10 μg/L, total national costs to community water systems will be $172.3 million (1999 dollars) annually at a 3% discount rate or $196.6 million annually at a 7% discount rate (U.S. EPA, 2001b). The annual average household cost increase for those systems requiring treatment is estimated to be $31.85 (1999 dollars) (U.S. EPA, 2001b).

1.2 Statement of the Problem

The current MCL for arsenic was primarily a concern for specific regions of the United States, and most utilities reported levels far below the existing standard of 50 μg/L, thus requiring no treatment. Compliance with an MCL of 10 μg/L will be a greater problem for utilities throughout the U.S., especially for smaller systems with limited financial resources. Many small groundwater systems which previously have required no treatment, will now require installation, operation, and maintenance of a treatment facility.

Most practicing engineers that are involved in the design process or regulatory approval process for small drinking water systems are not able to attend national conferences or workshops on emerging treatment technologies or regulations due to time or budget constraints. Therefore, the technologies for removal of arsenic may not be familiar to these engineers. Additionally, there has not been a demand for engineers to design arsenic removal systems due to the lack of systems exceeding the current MCL. Therefore, there is likely a general lack of knowledge among practicing engineers as to what treatment technologies may be appropriate for arsenic removal. This document intends to give guidance to small drinking water utilities, practicing engineers, and state and federal regulators on the treatment technologies that are available for arsenic removal and the wealth of information that is currently available on these technologies within the drinking water community.

1.3 Objectives of the Project

The objectives of this project are to produce an educational CD-ROM on arsenic removal water treatment technologies, which will target an audience consisting of state and federal regulators, practicing engineers, and small water system managers and operators. The CD-ROM includes multimedia features such as interactive process diagrams, video clips, photos, and sample plans of typical processes to aid in the understanding of the technologies by the user. The CD-ROM contains much of the narrative text of this thesis, including the literature review on arsenic removal, but does not include the discussion of the approach and process that was undertaken to create the CD-ROM. The CD-ROM will benefit engineers working on small arsenic removal systems by providing a comprehensive document on treatment technologies, and references to studies that were conducted on the subject, that will be easily obtainable and accessible.

CHAPTER 2

REVIEW OF THE LITERATURE

There is a current need for the compilation of information available on arsenic removal from drinking water. The following literature review will serve as a review of the available literature and provide references for readers wishing to research the topic further. The literature review will cover several topics involving arsenic removal including: regulatory history, occurrence data, chemistry review, health effects, treatment technologies, costs, and waste disposal alternatives. The focus in the treatment technology portion will be towards technologies available for use by small community water systems (serving approximately 10,000 people or less). Articles referenced in the literature review were identified by a computerized library database search using key words. Many of the articles were found from references cited in previously discovered articles.

2.1 Arsenic Regulation Development

Development of a National Interim Primary Drinking Water Regulation for arsenic has been delayed several times over the past 15 years because of uncertainties regarding health issues and the costs associated with compliance with a new rule (Pontius, 1995). Arsenic was first regulated in 1942 by the U.S. Public Health Service, which set a maximum limit at 50 μg/L for interstate water carriers (U.S. EPA, 2000d). The Safe Drinking Water Act (SDWA) of 1974 required that U.S. EPA set primary and secondary drinking water standards and, as a result, EPA issued a National Interim

Primary Drinking Water Regulation for arsenic of 50 μg/L in 1975. The 1986 amendments to the SDWA converted the 1975 interim arsenic standard to a National Primary Drinking Water Regulation (NPDWR) that was to be revised by the EPA by 1989. EPA has since deferred the revised regulation in order to better characterize the health risks and to determine the cost-effective technologies for small utilities (U.S. EPA, 2000d). Currently, and until a more stringent MCL is effective, the arsenic MCL in the United States is 50 μg/L and there is no maximum contaminant level goal (MCLG).

The World Health Organization (WHO) established a provisional guideline value for arsenic of 10 μg/L in their 1993 edition of *WHO Guidelines for Drinking-water Quality*. The Guidelines were developed for use as a "basis for the development of national standards in the context of local or national environmental, social, economic, and cultural conditions." The WHO (1999) states that the 10 μg/L arsenic guideline "would be even lower if not for lack of suitable testing methods." The Practicle Quantitation Limit (PQL), which defines the lowest concentration of an analyte that can be reliably measured within specified limits of precision and accuracy, is 3 μg/L for arsenic. The WHO standard is solely based on health effects and primarily on assessment of arsenic-induced skin cancer. Cancer risk estimates are the primary driving force behind the lowering of existing arsenic guidelines and the MCL in the United States (Pontius *et al.*, 1994).

In the 1996 amendments of the Safe Drinking Water Act (SDWA), Congress directed the U.S. EPA to propose a revised NPDWR for arsenic by January 1, 2000 and to issue the final regulation by January 1, 2001. In June 2000, the U.S. EPA issued a proposed arsenic rule in the *Federal Register* (U.S. EPA, 2000d). They proposed an

MCL for arsenic of 5 μg/L and requested comments on 3 μg/L, 10 μg/L, and 20 μg/L. Also, they proposed to set the MCLG, or non-enforceable goal, at zero. The final rule statutory deadline was then amended to June 22, 2001 by Congress (Water Tech Online, 2000). In January of 2001 EPA issued the final arsenic rule with an MCL of 10 μg/L and an MCLG of zero. This is only the second drinking water regulation which will set a standard less stringent than technically feasible level (3 μg/L based on treatment technologies and analytical methods) because EPA determined that the benefits of an MCL set at the feasible level would not justify the costs (the first time was in the final rule on uranium published on December 7, 2000) (U.S. EPA, 2001b). The regulation applies to non-transient non-community water systems, which are not presently subject to standards on arsenic, and to community water systems. The compliance date for requirements related to the final rule on arsenic is January 23, 2006.

At the time of writing this document, the EPA, under a new administration, decided to withdraw the new arsenic rule pending further study on the science and costs involved in its implementation. In April 2001 press releases, EPA Administrator Christie Whitman stated that the review of the final rule will be complete within a nine-month period and the agency does not intend to delay the compliance date of January 23, 2006 for a new MCL.

2.2 Health Effects

Arsenic ingestion has been linked to a multitude of health effects, both cancerous and non-cancerous. These health effects include cancer of the bladder, lungs, kidney, skin, nasal passages, liver, and prostate. Arsenic ingestion has also been attributed to

cardiovascular, pulmonary, immunological, and neurological, endocrine effects (U.S. EPA, 2001b).

The health effects of arsenic can be grouped into two categories; acute (short-term) and chronic (long-term) exposure. The acute toxicity effects of arsenic are well documented, however, drinking water engineers, are most interested in the chronic effects of arsenic in drinking water at low levels. This long-term effect is what the U.S. EPA's (2000d) revised MCL is based upon.

The actual toxicity of arsenic to the human body varies depending on several factors such as the general health of the individual and their diet. It is a cumulative substance, which slowly passes out of the body through urine, hair, fingernails/toenails and skin (Karim, 2000). Humans are exposed to arsenic primarily from air, food, and water. After ingestion, inorganic arsenic that is not immediately excreted or absorbed by tissues is progressively detoxified through the methylation process. The metabolism of arsenic in the human body involves two processes: (1) As(V) enters a cell and is reduced to As(III), and (2) As(III) is then methylated (i.e., chemically bonded to a methyl group, which is a carbon atom linked to three hydrogen atoms) to form the metabolites monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) which occurs primarily in the liver. In contrast to inorganic arsenic, neither MMA nor DMA binds strongly to biological molecules in humans, therefore their relative acute toxicity is less than that of inorganic arsenic forms. Given that arsenic can be detoxified in the body suggests that there is a level of exposure below which no adverse health effect would be observed. Any arsenic exposure above this level would only be partially detoxified, and adverse effects, commensurate with exposure, would be expected (Pontius *et al*., 1994). However, recent

work has shown that the assumption that organic forms that arise during the metabolism of inorganic arsenic are less toxic than inorganic forms may not be correct. This may indicate that the metabolism of inorganic arsenic is not necessarily a detoxification process. As yet, it is not known which form of arsenic participates in the key events within human cells that disrupt cell growth control and initiate or influence tumor formation (U.S. EPA, 2001b).

Health effects from consuming arsenic contaminated drinking water at the low-levels normally encountered are delayed. The most common signs of long-term, low-level arsenic exposure are dermal, or skin changes. These may include variations in skin pigmentation, hyperkeratoses, and ulcerations (Pontius *et al.*, 1994). Skin lesions are generally first, and appear after a minimum exposure of approximately 5 years (WHO, 1999). Development of peripheral vascular disease (hardening of the arteries to the arms and legs, that can cause pain, numbness, tingling, infection, gangrene, and clots) following exposure to inorganic arsenic in drinking water has also been reported (U.S. EPA, 2000d).

Inorganic arsenic is classified as a human carcinogen by the EPA based on sufficient evidence from human data (U.S. EPA, 1998). Increased lung cancer mortality was observed in multiple human populations exposed primarily through inhalation. Also, increased mortality from multiple internal organ cancers (liver, kidney, lung, and bladder) and an increased incidence of skin cancer were observed in populations consuming drinking water high in inorganic arsenic. Until the late 1980's, skin cancer was thought to be the only cancer associated with arsenic in drinking water. However, Asian, Mexican and South American populations with exposures to arsenic in drinking water at

or above several hundred micrograms per liter are reported to have increased risks of bladder and lung cancer along with skin cancer (U.S. EPA, 2000d).

EPA's Integrated Risk Information System (IRIS) database (U.S. EPA, 1998) provides an oral Reference Dose (RfD) for inorganic arsenic of 3×10^{-4} mg/kg-day. The RfD is defined as "an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime." Data from a study in 1977 by W.P. Tseng in an area of Taiwan with high concentrations of arsenic in drinking water was used to develop the RfD.

EPA based its toxicity analysis and risk level assessment in the final rule (U.S. EPA, 2001b) for arsenic on epidemiological studies and not on animal studies. Normally, the characteristics of human carcinogens can be explored and experimentally defined in animals. However, arsenic presented unique problems in EPA's risk assessment because there is no test animal species in which to study its carcinogenicity. Test animals do not appear to respond to inorganic arsenic exposure in a way that would make them useful as a model for human cancer assessment. Test animals metabolism of inorganic arsenic is quantitatively different than humans (U.S. EPA, 2001b).

The EPA has historically considered a risk range of 10^{-4} to 10^{-6} (1 in 10,000 to 1 in 1,000,000) as a target risk range protective of public health in its drinking water program (U.S. EPA, 2001b). In doing this, the EPA has sought to ensure that drinking water standards were established at levels such that less than 10% of the exposed population faced a risk that exceeded the chosen risk level. Current research on arsenic exposure has only been able to provide enough information to conduct a quantitative assessment of

bladder and lung cancers. Skin cancer was considered only qualitatively because of the difficulty in determining its endpoint, due to the fact that in the U.S. it is considered curable. In the final rule (U.S. EPA, 2001b) EPA based its evaluation of the risk posed by arsenic at each of the MCL options listed in the proposed rule on assessment of lung and bladder cancers. Table 1 (all tables referred to in the text are located in Appendix A) shows the cancer risks for exposed populations at several MCLs which EPA considered in developing a final rule. At 10 μg/L, the cancer risk for U.S. populations exposed at or above the MCL, after treatment, was found to be 0.63 to 2.99 X 10^{-4} (1 in 15,873 people to 1 in 3,344 people). The range of estimates accounts for the before and after adjustments for exposure uncertainty in documented studies (Taiwan study by Tseng) for arsenic in cooking water and food. At a final MCL of 10 μg/L, EPA estimates 21 to 30 fatal bladder and lung cancers and 12 to 26 non-fatal bladder and lung cancers per year are prevented (U.S. EPA, 2001b).

2.3 Arsenic Chemistry

A review of the chemistry of arsenic is necessary to understand the treatment technologies that are efficient in its removal from drinking water. Arsenic is a metalloid, which means it exhibits both metallic and nonmetallic chemical and physical properties. The oxidation state, or valence state, which is the capacity of the atom to combine with other atoms, is used to denote the form of arsenic present. Arsenic and its compounds are mobile in the environment. The "mobility" of arsenic in the environment means that it has the ability to enter a cycle of transport between land, air, and water under favorable conditions. In the case of groundwater, arsenic is able to migrate from the soil/rock

matrix to groundwater where geochemical conditions favor arsenic dissolution. Weathering of rock converts arsenic sulfides to arsenic trioxide, which enters the arsenic cycle as dust or by dissolution in rain, rivers, or groundwater. Water is the primary means of arsenic transport in the environment (Pontius *et al*., 1994).

Arsenic can occur in four oxidation states in water (-III, 0, +III, +V), but generally is found in only the trivalent (arsenite) and pentavalent (arsenate) states. The weak acids – arsenious acid, $HAsO_2$ (+III oxidation state or arsenite form), and arsenic acid, H_3AsO_4 (+V oxidation state or arsenate form) – will occur in the aqueous phase. Arsenious acid can speciate in five forms as $H_4AsO_3^+$, H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-}. Arsenic acid species are H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^2$, and AsO_4^{3-}. In natural waters, the valence and the species of arsenic present are dependent on oxidation-reduction conditions and the pH of the water. Arsenite forms are more likely to be found in oxygen-free (anaerobic) groundwater, while arsenate form are more common in aerobic surface waters (Harper and Kingham, 1992). Figures 1 and 2 (all figures mentioned in the text are located in Appendix B) show the solubility diagrams of As(III) and As(V), respectively. The figures indicate that for As(III), neutral forms exist at pH < 9.0 and the anionic forms exist at pH > 9.0. For As(V), anionic forms dominate at pH > 3.0 (U.S. EPA, 2000b,e,f). At the range of pH between 6 and 9, the primary arsenite species found in natural waters is H_3AsO_3. At this range of pH, the primary arsenate species found in groundwater are monovalent $H_2AsO_4^-$ and divalent $HAsO_4^{2-}$.

The observed coexistence of both As(III) (reduced form relative to As(V)) and As(V) (oxidized form) forms in surface waters is probably caused by the slow oxidation kinetics of arsenite to arsenate or bacterial reduction of arsenate to arsenite at neutral pH in

localized areas where a reducing environment can exist (Gupta and Chen, 1978; Waypa *et al*., 1997).

As(III) is more toxic to biological systems than is As(V) and it is also the more difficult form to remove using conventional treatment processes and adsorption techniques. This is because most removal mechanisms involve sorption of the negatively charged arsenate species to a positively charged surface, and arsenite exists primarily as a neutral species in natural waters (McNeill and Edwards, 1997b). Oxygen alone has been shown to have very slow reaction kinetics in oxidizing As(III) to As(V). Conventional oxidants used in drinking water treatment, such as chlorine, ozone, and permanganate, are capable of rapidly oxidizing As(III) to As(V) (Hering *et al*., 1996).

Iron and manganese are a strong influence on arsenic concentrations in the environment. Manganese oxide, which is common in freshwater sediments, is a very effective oxidant with respect to As(III) (Oscarson *et al*., 1981). In natural waters, As(V) fate and transport are intimately associated with iron oxides (McNeill and Edwards, 1997a). Arsenic can be immobilized through adsorption-coprecipitation with iron and manganese hydroxides, or mobilized when such solids are dissolved under reducing conditions, or released from the oxide surfaces in the event of competition (for sorptive surface sites) in the presence of orthophosphate and natural organic matter (NOM) (Edwards, 1994).

It is important to know the valence state and species of arsenic in the source water prior to design of any arsenic treatment system. Treatment processes such as coagulation/filtration and lime softening rely on adsorption and coprecipitation of arsenic to metal hydroxides, thus the valence state must be known for effective removal. Also,

processes such as anion exchange and activated alumina function by exchanging arsenate with counter ions of an anionic resin and by adsorbing arsenate onto alumina, respectively, thus the valence state must be known to design an effective treatment system.

2.4 Arsenic Occurrence

The contamination of a drinking water source by arsenic can result from either natural or human activities. Arsenic is an element that occurs naturally in rocks and soil, water, air, plants, and animals. Natural sources that can release arsenic into the environment include volcanic activity, the erosion of rocks and minerals, and forest fires. Arsenic is used for a variety of industrial purposes: electrophotography, catalysts, pyrotechnics, antifouling paints, pharmaceutical substances, dyes and soaps, ceramics, alloys, battery plates, and semiconductors. Inorganic arsenic and its compounds are used as a wood preservative to pressure treat lumber and was used, until voluntarily canceled in 1993, as an agricultural pesticide. The production of chromated copper arsenate, an inorganic arsenic compound and wood preservative that has been used for more than 60 years, accounts for approximately 90% of the arsenic used annually by industry in the United States (Welch *et al.*, 2000; U.S. EPA, 2000d).

As discussed in the chemistry review section, the presence of iron oxides in groundwater has a dramatic affect on the mobility and concentration of arsenic. Reduction and dissolution of iron oxide through reaction with organic matter appear to produce high arsenic groundwater in some parts of the country. This appears to be the most common cause of regionally high arsenic concentrations (Welch *et al.*, 2000). Most

of the high concentrations of arsenic in the western U.S. can be attributed to weathered volcanic rocks, geothermal areas, irrigation practices, or mineral deposits (Korte, 1991). Table 2 shows a summary of some of the most important reactions affecting arsenic concentrations in groundwaters listed by Welch et al. (2000).

Korte (1991) describes a common set of hydrogeologic conditions that yield elevated levels of naturally occurring arsenic in groundwaters of the midwestern United States. When investigating the groundwater at an industrial facility in Missouri he found arsenic levels exceeding 50 μg/L with no historical usage of arsenic at the facility. He found that the high concentration of arsenic in some of the wells was due to the desorption from iron oxides under reducing conditions and subsequent mobilization into the groundwater. The mechanism probably begins with the deposition of iron oxides during streamflow while the alluvium is being deposited. The oxides, which have a strong affinity for dissolved arsenic, adsorb it from the streamflow. As the alluvium is being buried, it eventually becomes subject to slow groundwater movement. As redox conditions become increasingly reducing, the ferric iron is reduced to ferrous iron, resulting in mobilization of some of the adsorbed arsenic. Korte's conclusion was that the high occurrences of arsenic are sporadic because the arsenic is mobilized only under a narrow range of redox conditions. Localized variations in potential (Eh) and arsenic content lead to varying arsenic levels.

A key component of recent literature on arsenic removal is the assessment of the number of water systems that will be expected to exceed the new MCL and thus require some type of treatment. Frey and Edwards (1997) synthesized three surveys of arsenic occurrence in the U.S. – the National Arsenic Occurrence Survey (NAOS), the National

Inorganics and Radionuclides Survey (NIRS), and a survey by the Metropolitan Water District of Southern California (MWDSC). They drew several conclusions from the study, including: (1) overall, higher concentrations of arsenic are present in groundwater sources compared with surface water sources, (2) the majority of water sources, 53-71% of groundwater sources and 61-88% of surface water sources, were found to have arsenic present below 2 μg/L, (3) regional trends in arsenic occurrence were found for both surface water and groundwater sources, with higher concentrations of arsenic in the south central and more western states, and (4) between 6 and 17% of systems (2,775 - 7,870) were projected to have arsenic levels >5 μg/L.

The U.S. Geological Survey (USGS) published a study of arsenic occurrence in the U.S. using data collected over the last two decades of potable water from 18,850 wells in 595 counties across the United States (USGS, 2000). Their data are depicted in Figures 3 and 4. Analysis of the USGS data indicates that arsenic concentrations are generally highest in the Western U.S. High concentrations were also found in parts of the Midwest and Northeast at levels exceeding 10 μg/L. The USGS estimated that just over 7.6% of small systems (serving between 1,000 and 10,000 persons) used water with arsenic concentrations greater than 10 μg/L, compared to fewer than 1% exceeding the current 50 μg/L MCL.

The EPA used compliance monitoring data from the "25-States database" to establish occurrence and exposure distributions of arsenic in public groundwater and surface water supplies (U.S. EPA, 2000d). The database provided finished water data for arsenic from over 77,000 observations from more than 26,600 public water systems in 25 states. States for which EPA had no data were accounted for by assigning regional occurrence

distributions to them (U.S. EPA, 2001b). Table 3 shows a comparison of estimates from NAOS, NIRS, USGS, and the proposed and final EPA rules, of systems that are exceeding arsenic concentrations at levels of 2, 3, 5, 10, and 20 μg/L (U.S. EPA, 2001b). EPA estimates that 5.3% and 0.8% of groundwater CWSs and surface water CWSs, respectively, have average arsenic levels above 10 μg/L. This corresponds to approximately 2,300 CWSs (out of a total of 43,749 systems) using groundwater and 85 CWSs (out of a total of 10,683 systems) using surface water that will exceed the new 10 μg/L MCL. An estimated 1,100 NTNCWS (out of 20,000 systems nationwide) will also exceed the 10 μg/L MCL and will require treatment.

2.5 Treatment Technologies

Compliance with a revised arsenic MCL will be required for community water systems once the pending final rule is published and following a likely five-year compliance schedule. Thus, large and small utilities alike must begin to formulate a strategy for coming into compliance with a more stringent MCL. It is assumed that most utilities with existing treatment processes in place will attempt to enhance those processes to attain compliance if feasible. However most systems using groundwater currently have no treatment scheme in place. Therefore, these systems, if in non-compliance with the new MCL, will be required to install a new treatment system for arsenic removal. The best arsenic treatment technique for a given utility will depend on the arsenic concentration and species in the feedwater, co-occurring constituents in the water, existing treatment processes, treatment costs, and the handling of any residuals (Chen *et al.*, 1999).

In the final rule on arsenic, the EPA (2001b) identified Best Available Technologies (BATs) for arsenic removal based on the following criteria:

(1) the capability of a high removal efficiency;

(2) a history of full-scale operation;

(3) general geographic applicability;

(4) reasonable cost based on large and metro water systems;

(5) reasonable service life;

(6) compatibility with other treatment processes; and

(7) the ability to bring all of the water in a system into compliance.

The BATs identified, which are shown in Table 4, are ion exchange, activated alumina, reverse osmosis, modified coagulation/filtration, modified lime softening, electrodialysis reversal, and oxidation/filtration. EPA also listed several technologies that are considered affordable and applicable to typical small drinking water systems (serving less than 10,000 people) which are listed in Table 5. These technologies are: activated alumina (centralized and point-of-use(POU)), coagulation/filtration, coagulation-assisted microfiltration, electrodialysis reversal, enhanced coagulation/filtration, enhanced lime softening, ion exchange, lime softening, oxidation/filtration, and reverse osmosis (centralized and POU). A summary of reported performance of the various technologies from the literature is shown in Table 6. Table 7 summarizes many of the advantages and disadvantages of each of the technologies.

2.5.1 Enhanced Coagulation/Filtration and Coagulation/Microfiltration

Coagulation/filtration is a commonly-used treatment process for removing turbidity in the form of suspended and dissolved solids from surface waters. Many of the systems using this process tend to be larger surface water systems; however, there are some small groundwater coagulation/filtration plants (~8% of small groundwater systems). When the lower arsenic MCL takes effect, it is anticipated that most of these systems with treatment in place will attempt to meet the new standard through modification of existing treatment, resulting in the least cost alternative for these facilities. Enhanced coagulation involves modification to the conventional coagulation/filtration process either by increasing the coagulant dosage, reducing the pH, or both to increase arsenic removal. A typical process diagram using coagulation/filtration can be seen in Figure 5. Coagulation/microfiltration involves replacing the conventional gravity filter with a microfiltration membrane separation process to increase sorbed arsenic removal.

In most water treatment literature coagulation is an all-encompassing term referring to the chemical and physical processes bringing about aggregation of particles in water treatment. The aggregation forms flocs which can then be removed by sedimentation and filtration. A typical coagulation/filtration treatment train has four steps: (1)chemical coagulant addition – rapid mixing unit where chemical dispersal and particle destabilization take place, (2)flocculation – slow mixing units where interparticle collisions take place and the particles agglomerate, (3)sedimentation, and (4)filtration. The most common coagulants used in the drinking water industry are alum and iron (III) salts. In addition to its typical use for removing turbidity causing particles from water,

the process can also remove dissolved inorganics such as arsenic by mechanisms discussed below (U.S. EPA, 2000b).

The primary removal mechanisms for arsenic during coagulation/filtration are adsorption, precipitation, and coprecipitation or occlusion in the precipitated solids (Edwards, 1994; Ferguson and Anderson, 1974; U.S. EPA, 2000b). Adsorption refers to the formation of surface complexes between soluble arsenic and the amorphous metal hydroxide solid. Precipitation refers to the insolubilization of the arsenic by exceeding a solubility product, which is either $Fe(AsO_4)$ or $Al(AsO_4)$ solids. Coprecipitation incorporates the soluble arsenic into a growing hydroxide phase (Edwards, 1994). At high coagulant dosages, adsorption of inorganic contaminants (arsenic) to precipitated metal hydroxide solids is likely to be the predominant mechanism for contaminant removal (Hering *et al.*, 1996).

Removal efficiency of arsenic is a function of the oxidation state of arsenic, the type of coagulant and its dosage, the pH of the water, and the initial arsenic concentration (Sorg and Logsdon, 1978). However, other researchers have concluded that the initial concentration is not a factor in arsenic removal efficiency at levels typically encountered in drinking water treatment (Hering *et al*., 1997). This lack of dependence on initial concentration is explained by the adsorption behavior of arsenic to the surface of the freshly precipitated and unsaturated metal hydroxide. Temperature and competing anions such as sulfate and natural organic matter (NOM) also affect arsenic removal (McNeill and Edwards, 1997a). As with several of the treatment technologies used for arsenic removal, arsenic in the +V oxidation state is much more efficiently removed by coagulation. Cheng *et al*. (1994) described three important points in comparing alum and

ferric chloride ($FeCl_3$) arsenic removal from bench and pilot-scale data: (1) $FeCl_3$ is more effective than alum; (2) alum is pH-dependent, and the highest As(V) removals are achieved at pH < 7.0; and (3) $FeCl_3$ coagulation is not pH-dependent between 5.5 and 7.0, but increasing coagulant dosage will increase As(V) removal. The better removal by the ferric chloride as compared to the alum is thought to be because of better removal of $Fe(OH)_3$ flocs versus $Al(OH)_3$ flocs during filtration (McNeill and Edwards, 1997a) and incomplete precipitation of added aluminum as the amorphous hydroxide solid . Removal percentages are better for ferric chloride compared to alum only on a weight basis (mg/L) and are said to be equal to alum on a molar basis at pH < 7.5 (Edwards, 1994).

McNeill and Edwards (1997a) developed a hierarchy to improve arsenic removal at coagulation/filtration facilities not meeting the MCL. The hierarchy is as follows: (1) oxidize any As(III) in the raw water to As(V) (potassium permanganate addition and chlorination have been shown to be successful and ozonation and hydrogen peroxide may be effective pending further study); (2) for alum plants, minimize residual soluble Al by increasing the precipitation of $Al(OH)_3$ which sorbs the arsenic; and (3) increase the coagulant dosage or consider changing coagulant type.

McNeill and Edwards (1997a) also developed a model to predict the As(V) removal efficiency of coagulation/filtration plants. The model is similar to a Langmuir isotherm and is independent of As(V) concentration. For plants using ferric chloride as a coagulant the following equation applies:

$$\text{As(V) removed (\%)} = 100 \cdot \frac{78 \cdot \left(\text{FeCl}_3 \text{ dosage in } \frac{\text{mg}}{\text{L}} \right) \cdot \left(\frac{\text{mmoles Fe}}{162.5 \text{ mg FeCl}_3} \right)}{1 + 78 \cdot \left(\text{FeCl}_3 \text{ dosage in } \frac{\text{mg}}{\text{L}} \right) \cdot \left(\frac{\text{mmoles Fe}}{162.5 \text{ mg FeCl}_3} \right)} \qquad \text{Equation 1}$$

The following example calculation illustrates the use of the above equation:

Given: Ferric chloride coagulation plant

$FeCl_3$ dose = 10 mg/L

Influent As = 30 µg/L

Required: Effluent arsenic concentration

Solution:
$$\text{As(V) removed (\%)} = 100 \cdot \frac{78 \cdot \left(10 \frac{\text{mg}}{\text{L}} \cdot \frac{\text{mmoles Fe}}{162.5 \text{ mg FeCl}_3} \right)}{1 + 78 \cdot \left(10 \frac{\text{mg}}{\text{L}} \cdot \frac{\text{mmoles Fe}}{162.5 \text{ mg FeCl}_3} \right)}$$

As removed (%) = 82.8%

$$\text{Effluent As} = \text{Influent As} \times (1 - 0.828)$$

$$\text{Effluent As} = 30 \text{ µg/L} \times (1 - 0.828)$$

Effluent As = 5.16 µg/L

At plants using alum as the coagulant, the following equation applies which also takes into account arsenic sorbed onto particulate iron in the source water:

$$\text{As(V) removed (\%)} = 100 \cdot \frac{\left[78 \cdot \left(\text{particulate Fe} \frac{\text{mg}}{\text{L}} \cdot \frac{\text{mmoles Fe}}{56 \text{ mg Fe}} + \text{alum dose} \frac{\text{mg}}{\text{L}} \cdot \frac{2 \text{ mmoles Al}}{660 \text{ mg alum}} \right) \right]}{\left[1 + 78 \cdot \left(\text{particulate Fe} \frac{\text{mg}}{\text{L}} \cdot \frac{\text{mmoles Fe}}{56 \text{ mg Fe}} + \text{alum dose} \frac{\text{mg}}{\text{L}} \cdot \frac{2 \text{ mmoles Al}}{660 \text{ mg alum}} \right) \right]} \qquad \text{Equation 2}$$

The following example calculation illustrates the use of the above equation:

Given: Alum coagulation plant

Influent particulate Fe = 0.6 mg/L

Alum dose = 30 mg/L

Influent As = 30 μg/L

Required: Effluent As

Solution:

$$\text{As(V) removed (\%)} = 100 \cdot \frac{\left[78 \cdot \left(0.6\frac{\text{mg}}{\text{L}} \cdot \frac{\text{mmoles Fe}}{56\text{ mg Fe}} + 30\frac{\text{mg}}{\text{L}} \cdot \frac{2\text{ mmoles Al}}{660\text{ mg alum}}\right)\right]}{\left[1 + 78 \cdot \left(0.6\frac{\text{mg}}{\text{L}} \cdot \frac{\text{mmoles Fe}}{56\text{ mg Fe}} + 30\frac{\text{mg}}{\text{L}} \cdot \frac{2\text{ mmoles Al}}{660\text{ mg alum}}\right)\right]}$$

As removed (%) = 88.8%

$$\text{Effluent As} = \text{Influent As} \times (1 - 0.888)$$

$$\text{Effluent As} = 30\,\mu\text{g/L} \times (1 - 0.888)$$

Effluent As = 3.36 μg/L

The models defined in Equations 1 and 2 predict arsenic removal to within ±13% (90% confidence) for iron coagulation at pH 6.5-8.0 and alum coagulation at pH < 7.6 if all possible sources of particulate iron and aluminum hydroxide present in the system are accounted for. The adsorption rate constant or, "K" value, given above as 78 mM^{-1}, is an average value derived from best fit of the data for a number of utilities and is meant to be used only to calculate an estimate of arsenic removal (McNeill and Edwards 1997a). A

better prediction of arsenic removal could be achieved if a utility were to derive an individual "K" value from their raw water quality and plant conditions.

Coagulation assisted microfiltration is a process that is presently being researched as an arsenic removal technology. The process is essentially the same as the conventional coagulation/filtration scheme except that the standard gravity filter is replaced by a microfiltration membrane process. The microfiltration process gives the added advantage of being able to remove much smaller flocs and particles than the conventional gravity filter, thus increasing the removal of arsenic sorbed flocs. It also can give the secondary advantage of acting as a barrier to microorganisms and increasing total plant capacity (U.S. EPA, 1999). Utilities that have existing coagulation/filtration treatment and are unable to use higher coagulant dosages may be able to use microfiltration to increase the removal of total arsenic by increasing the removal of particulate arsenic. Systems that have removed between 53 and 92% arsenic using conventional coagulation/filtration, have been able to remove more than 97% using microfiltration (Frey *et al*., 1998). Plans are currently underway to construct a 2.3 MGD facility using coagulation/microfiltration processes for arsenic removal from groundwater at Albuquerque, N.M. Albuquerque's raw water arsenic ranges from < 2 μg/L to > 50 μg/L, and based on data from pilot testing of the water, will be able to reduce the arsenic concentrations to < 2 μg/L (Chwirka *et al*., 2000).

There are a number of studies in the literature on the removal of arsenic by coagulation/filtration of source waters. Bench-scale tests by Hering *et al*. (1997) achieved close to or better than 80% removal over the pH ranges of 4.0 to 8.0 with ferric chloride (4.9 mg/L $FeCl_3$) and pH ranges of 6.0 to 8.0 with alum [40 mg/L

$Al_2(SO_4)_3 \cdot 18H_2O$]. Scott *et al.* (1995) studied a full-scale conventional coagulation plant and found that a dose of 3-10 mg/L of ferric chloride achieved removals of 81-96% and doses of 6-20 mg/L of alum achieved removals of 23-71%. Ferric coagulation reduced the levels from 1.6 μg/L in the influent to 0.07-0.32 μg/L in the filtered effluent. Alum coagulation reduced the levels from 2.15 μg/L to 0.66-1.65 μg/L. McNeill and Edwards (1995) study of full-scale alum coagulation plants showed very low removal percentages (<50%) with dosages of 10 mg/L alum. This study of alum coagulation provided a possible explanation for the poor removal efficiencies in that either there was an inadequate amount of particulate aluminum present for arsenic sorption or, the aluminum flocs with sorbed arsenic were too small to be removed by filtration. The EPA (2000b) studied two existing full-scale conventional coagulation/filtration plants and found that they could consistently achieve low levels (< 5 μg/L) of arsenic in finished water. Average removal percentages found were 52% (reduction in As concentration from 7.5 μg/L to 3.5 μg/L) and 79% (reduction in As concentration from 19.1 μg/L to 4.0 μg/L). A prevailing theme throughout much of the coagulation/filtration literature is that efficient filter performance is necessary for high arsenic removal. Increased arsenic concentrations can occur in the finished water due to breakthrough of colloidal particles, with which arsenic may be associated, if filtration is not operating efficiently (Hering *et al.*, 1996).

2.5.2 Enhanced Lime Softening

Lime softening is a process commonly used in the drinking water industry for reducing hardness in source waters. Hardness in water can primarily be attributed to

calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions. Addition of lime to the source water provides a hydroxide ion which increases the pH and results in the precipitation of calcium carbonate, $CaCO_3$, and magnesium hydroxide, $Mg(OH)_2$. The process can also remove arsenic from the source water if operated under ideal or "enhanced" conditions. Enhanced lime softening is defined as softening to pH>10.5 and causing $Mg(OH)_2$ precipitation (McNeill and Edwards, 1995). Typical lime softening plants consist of rapid mix, flocculation, sedimentation, and filtration units. A typical lime softening process diagram can be seen in Figure 6.

The primary mechanism for removal of As(V) during lime softening is coprecipitation with the $Mg(OH)_2$ (U.S. EPA, 2000b). Arsenic removal efficiencies with a pH high enough to precipitate magnesium hydroxide can be as high as 90%, while efficiencies with only calcium carbonate precipitation can be as low as 0-10% (McNeill and Edwards, 1995). Removal efficiencies are highly dependent upon pH and the valence state of the arsenic. Efficiencies increase with increasing pH, with an optimum pH at 10.5 and above (Sorg and Logsdon, 1978). As is the case with other treatment technologies, As(V) is more efficiently removed with lime softening than As(III), therefore if As(III) is present at high levels, preoxidation will be required.

McNeill and Edwards (1997b) developed a hierarchy for existing lime softening plants which are unable to meet the arsenic MCL. Three options were presented: (1) if arsenite is present, then oxidize to arsenate (this can be accomplished with permanganate or chlorination as discussed previously); (2) utilities which are currently precipitating only calcium carbonate can add a small amount of iron and dramatically increase arsenic

removal; and (3) raise the pH to precipitate magnesium hydroxide which will increase arsenate removal.

McNeill and Edwards (1997b) also developed a predictive model which accounts for the role of multiple solids [$CaCO_3$, $Mg(OH)_2$, and $Fe(OH)_3$] in arsenate removal during softening. The following equation, which includes dissolved arsenate as the only unknown, can be used to find the soluble arsenate concentration at a utility:

$$As_{sol} = \left[\frac{As_{tot}}{\left[1 + (K_{CaCO_3} \cdot Ca_{ppt}) + (K_{Mg(OH)_2} \cdot Mg_{ppt}) + (K_{Fe(OH)_3} \cdot Fe_{ppt})\right]} \right] \qquad \text{Equation 3}$$

where:

As_{sol} = Soluble arsenate concentration (µg/L)

As_{tot} = Influent arsenate concentration, equal to As_{sorbed} + As_{sol} (µg/L)

$K_{CaCO_3}, K_{Mg(OH)_2}, K_{Fe(OH)_3}$ = Sorption equilibrium constants determined in lab experiments [$(mg/L)^{-1}$]

Ca_{ppt}, Mg_{ppt}, Fe_{ppt} = Measured amounts of precipitates as calcium carbonate, magnesium hydroxide, and ferric hydroxide (mg/L as Ca^{+2}, Mg^{+2}, or Fe^{+3})

Percent removal can then be easily calculated given the total influent arsenate concentration. Individual adsorption constants were not given in the McNeill and Edwards paper, and thus must be determined in the lab for each source water that is to be studied.

A number of pilot-plant and full-scale studies have been conducted on lime softening plants to determine their feasibility for arsenic removal. The EPA (2000b) conducted a long-term study of a full-scale lime softening plant and found that it was only able to achieve 45% removal of total arsenic (reduction from 32.0 µg/L to 16.6 µg/L). However, the suspected cause of the inefficient removal was that the plant was

operating at a pH of 9.6, which wasn't high enough to precipitate magnesium hydroxide. Sorg and Logsdon's 1978 study of a lime softening pilot-plant showed nearly 100% removal of As(V) at levels of 400 μg/L and at a pH of 10.5 and above. McNeill and Edwards (1995) study of full-scale plants found that removal efficiencies of up to 90% could be obtained with magnesium hydroxide precipitation.

2.5.3 Iron Removal

Iron and manganese removal is a longstanding and generally reliable treatment process. The process consists of oxidation of iron and manganese in order to form a precipitate which can be removed by filtration. Iron and manganese can cause aesthetic problems with drinking waters at levels approximately at or above 0.3 mg/L for iron and 0.05 mg/L for manganese. The aesthetic problems may include colored water, turbidity, staining of laundry and bathroom fixtures, and astringent tastes. The conventional removal scheme consists of aeration, oxidant addition, sedimentation or detention, filtration and possibly other chemical additions (Robinson, 2000). A typical iron and manganese removal process diagram can be seen in Figure 7.

Arsenic removal can be accomplished along with iron and manganese removal. Two primary removal mechanisms are thought to control the removal of arsenic using iron removal: adsorption and coprecipitation. Several steps have been documented in the removal of arsenic using iron removal processes (U.S. EPA, 2000d) as follows: (1) the reduced iron, Fe(II) is oxidized to the relatively insoluble Fe(III) and any As(III) present is oxidized to As(V); (2) the As(V) attaches to the iron hydroxides through adsorption and/or coprecipitation; and (3) the precipitate is filtered from the water by rapid sand

filters or pressure filters. When the raw water contains As(III), sufficient contact time needs to be provided to convert the As(III) to As(V) for removal by the oxidation/filtration process. An additional preoxidation step is not required for this process as long as there is sufficient contact time (U.S. EPA, 2001b). However, it must be recognized that the oxidation kinetics of aeration for As(III) oxidation are very slow and it is recommended that an oxidant be added when As(III) is the primary species in the water.

Edwards (1994) described the removal of arsenic using iron removal process as being analogous to the coagulation process. The production of Fe-Mn species and subsequent precipitation of hydroxides in Fe-Mn removal processes are analogous to an in situ coagulant addition, with the quantity of Fe or Mn removed being the "coagulant dosage." McNeill and Edwards (1997a) developed a model predicting arsenic removal during metal hydroxide precipitation based on the feedwater iron and aluminum concentrations which is applicable to iron removal processes as well as the coagulation process described earlier. The model is essentially the same as presented earlier for enhanced coagulation/filtration, assuming there is very little aluminum in the raw water, and is described as follows:

$$\text{As(V) removed (\%)} = 100 \cdot \frac{\left[78 \cdot \left(\text{particulate Fe formed in } \frac{\text{mg}}{\text{L}} \cdot \frac{\text{mmoles Fe}}{56\,\text{mg Fe}}\right)\right]}{\left[1 + 78 \cdot \left(\text{particulate Fe formed in } \frac{\text{mg}}{\text{L}} \cdot \frac{\text{mmoles Fe}}{56\,\text{mg Fe}}\right)\right]} \qquad \text{Equation 4}$$

The following example calculation illustrates the use of the above equation:

Given: Iron removal plant

Particulate Fe formed after oxidation = 0.6 mg/L

Influent As = 30 μg/L

Required: Effluent As

Solution:

$$\text{As(V) removed (\%)} = 100 \cdot \frac{\left[78 \cdot \left(0.6 \frac{\text{mg}}{\text{L}} \cdot \frac{\text{mmoles Fe}}{56\,\text{mg Fe}}\right)\right]}{\left[1 + 78 \cdot \left(0.6 \frac{\text{mg}}{\text{L}} \cdot \frac{\text{mmoles Fe}}{56\,\text{mg Fe}}\right)\right]}$$

As removed (%) = 45.5%

$$\text{Effluent As} = \text{Influent As} \times (1 - 0.455)$$

$$\text{Effluent As} = 30\,\mu\text{g/L} \times (1 - 0.455)$$

Effluent As = 16.4 μg/L

The model can predict arsenic removal to within ±13% (90% confidence) if all possible sources of particulate iron and aluminum hydroxide present in the system are accounted for. The adsorption rate constant or, "K" value, given above as 78 mM^{-1}, is an average value derived from best fit of the data for a number of utilities and is meant to be used only to calculate an estimate of arsenic removal (McNeill and Edwards, 1997a). A better prediction of arsenic removal could be achieved if a utility were to derive an individual "K" value from their raw water quality and plant conditions.

EPA (2001b) listed oxidation/filtration as a BAT with a footnote that the iron-to-arsenic ratio must be at least 20:1. For the process to be efficient, the source water must have high iron content (in developing national cost estimates, EPA assumed that only systems with > 300 μg/L of iron would opt for this technology). If iron is not present at high levels, the oxidation and subsequent filtration of the feedwater is unlikely to remove sufficient arsenic (U.S. EPA, 2000d). For these reasons, it is assumed that systems using this technology for removal of arsenic will be those that have an existing treatment facility in place for iron removal, typically groundwater systems, and which don't require a high removal efficiency for arsenic.

Studies conducted by the EPA (2000e) of two existing full-scale iron removal plants showed varied results in the ability of the iron removal process to consistently achieve arsenic concentrations < 5 μg/L. Average arsenic removal efficiencies at the two plants were 87% (reduction from 20.3 μg/L to 3.0 μg/L) and 74% (reduction from 48.5 μg/L to 11.9 μg/L) respectively. The lower arsenic removal efficiency was thought to be the result of lower iron levels (1,137 μg/L versus 2,284 μg/L) in the source water. McNeill and Edwards (1995), using data obtained from full-scale iron and manganese removal plants, found that oxidation of Fe(II) resulted in 80-95% arsenic removal, when the Fe(II) in the feedwater was greater than 1.5 mg/L. They also found that plants which oxidize only Mn(II) did not remove significant concentrations of arsenic. Therefore they concluded that As(V) removal efficiency was controlled by Fe(II) oxidation and $Fe(OH)_3$ precipitation and not Mn(II) oxidation and manganese hydroxide precipitation.

2.5.4 Ion Exchange

The process of ion exchange is most often defined as the reversible exchange of ions between a solid and a liquid in which there is no substantial change in the structure of the solid. In ion exchangers used for treating drinking water, the liquid is the feedwater and the solid is typically a synthetic ion exchange resin which is used to preferentially remove certain contaminants of concern. The process is most widely used in drinking water treatment to soften water by exchanging calcium and magnesium ions for sodium ions. Ion exchange is also widely used to remove metals from industrial wastewater effluents (Wachinski and Etzel, 1997). A typical process diagram for ion exchange treatment can be seen in Figure 8.

Anion exchange resins come in two classes, strong base anion (SBA) and weak base anion (WBA). The most common SBA resins have quarternary ammonium functional groups ($-CH_2N(CH_3)_3Cl$) which are strongly basic and ionized to act as ion exchangers over the pH range of 0 to 13. WBA resins are useful only in the acidic pH range. SBA and WBA resins may be present in the hydroxide or the chloride form. SBA resins in the chloride form are typically used for arsenic removal because they tend to be more effective over a wider pH range. Synthetic resins are available in bead form and range in size from 20 mesh (0.84 mm in diameter) to 325 mesh (0.044 mm in diameter). Most ion exchange applications in water and wastewater are accomplished with resins in the 20 to 50-mesh size range (Wachinski and Etzel, 1997).

Ion exchange doesn't remove As(III) because As(III) occurs predominantly as an uncharged ion (H_3AsO_3) in water with a pH value of less than 9.0. However, the predominant species of As(V) at pH > 3.0 are negatively charged ($H_2AsO_4^-$, $HAsO_4^{2-}$, and

AsO_4^{3-}), and thus can be removed by ion exchange. Arsenate and several other anions are preferentially removed according to the order of preference for exchange by the resin (U.S. EPA, 2000f). The general selectivity sequence for the preferential removal of major ions by ion exchange is given by Chwirka *et al*. (2000) and is reported as:

$$SO_4^{2-} > HAsO_4^{2-} > CO_3^{2-} \text{ and } NO_3^- > Cl^- > H_2AsO_4^- \text{ and } HCO_3^- >> Si(OH)_4 \text{ and } H_3AsO_3 \qquad \text{Equation 5}$$

From the selectivity sequence for ion exchange resins, it can be seen that the process prefers sulfate to arsenic. This reveals the major problem with using ion exchange for removing arsenic from solution. The efficiency of the process is strongly affected by competing ions like total dissolved solids and sulfate. When the sulfate level is high in the feedwater, sulfate may displace previously sorbed ions (such as arsenate) from a resin bed, thereby causing higher arsenic concentrations in the finished water than in the feedwater. This is referred to as chromatographic peaking (dumping) and can be a risky situation where toxic ions like arsenic are involved (U.S. EPA, 2000f). To avoid this, the resin must be monitored and regenerated prior to the onset of peaking. Generally, the ion exchange process is not considered economically attractive if the feedwater contains high TDS (>500 mg/L) and sulfate (>150 mg/L) due to the frequency of resin regeneration required (Clifford, 1999). Clifford, as reported by EPA (2001a), estimated the bed volumes to 10% and 50% breakthrough of influent arsenic as a function of influent sulfate concentration. Figure 9 shows the relationship between sulfate

concentrations and bed volumes to breakthrough. EPA (2000d) recommends ion exchange as a BAT primarily for small, groundwater systems with low sulfate and TDS, and as a polishing step after filtration.

Wachinski and Etzel (1997) summarized the ion exchange process in four general steps: backwash, regeneration or brining, rinse, and service. The service step of the column is the operational mode of the system. The feedwater is passed downflow through a chloride-form SBA resin, and the chloride and arsenate exchange takes place according to the following reaction:

$$2\overline{RCl} + HAsO_4^{2-} \Rightarrow \overline{R_2HAsO_4} + 2Cl^- \qquad \text{Equation 6}$$

The end of the run is when a predetermined concentration of arsenic is reached in the effluent from the column. This is referred to as breakthrough. The column can then be taken off line to regenerate the resin before putting it back into service.

The backwash step involves the introduction of water in a countercurrent flow to the column at a rate sufficient to expand the bed by 50 – 75%. Its purpose is to remove accumulated silt, dirt, iron, etc., from the resin and to reorient and redistribute the resin beads.

Following backwash, the ion exchange resin can be regenerated by returning it to the chloride form and removing the contaminant anion. This step is usually accomplished by using a 3 – 12% sodium chloride solution for chloride form resins, with the result being essentially complete elution of arsenic from the spent resin at steady state operation (Clifford, 1999). The equation for regeneration of the SBA resin, in principle

the reverse of the previous equation except that a high chloride concentration is required to reverse the reaction, and is given by Clifford (1999) as the following:

$$\overline{R_2HAsO_4} + 2NaCl \Rightarrow 2\overline{RCl} + Na_2HAsO_4 \qquad \text{Equation 7}$$

Following the above equation, Clifford indicates that regeneration isn't difficult because the divalent ion arsenate is being replaced by the monovalent ion chloride in high ionic strength solution where electronegativity favors monovalent ion uptake by the resin. Countercurrent, upflow regeneration is usually practiced to minimize the contaminant leakage from the column. Leakage is the appearance of a low concentration of the contaminant ion in the column effluent initially after returning the bed to service. Such leakage isn't due to influent ions coming through the column without being exchanged, rather, it is due to residual ions in the resin at the bottom of the column as a result of incomplete regeneration (Anderson, 1975). However, Clifford (1999), found in an Albuquerque, N.M. field study that cocurrent regeneration performed better (it gave a lower arsenic leakage during subsequent exhaustions), thus making it unnecessary to use countercurrent (or upflow) regeneration to minimize arsenic leakage. Clifford explains that the reason for this was because, at exhaustion, most of the arsenic on the resin is concentrated in a thin zone near the column outlet. Thus results show that it is preferable to elute the arsenic by the shortest path as opposed to flushing it back through the entire resin bed, where some could possibly remain during upflow regeneration. Although Clifford doesn't explicitly say so, it is assumed that the more preferred anions such as sulfate are displacing the previously adsorbed arsenate higher in the column, thus

creating the thin zone near the column outlet. The brine used for regeneration can be recycled several times (at least 20 times and possibly more) prior to disposal with no loss of effectiveness, which gives the advantage of reducing volume of wastewater produced and reducing the volume of salt used for regeneration (Chwirka *et al*., 2000; Clifford, 1999).

After regeneration and prior to putting the column back into service, rinsing should be performed. The rinse step will remove any excess regenerant from the system (Wachinski and Etzel, 1997).

Pretreatment of the feedwater prior to the ion exchange unit should be considered under certain conditions. If high particulate iron concentrations are found in the feedwater, prefiltration should be used to prevent serious leakage of arsenic. Particulate iron will strongly adsorb As(V) and prevent ion exchange by the resin (Clifford, 1999). Also, high suspended solids in the feedwater can cause clogging of the ion exchange bed and would need to be removed by prefiltration. If analysis of the feedwater indicates that arsenic is present in the +III state, preoxidation by chlorination or other means will be required to convert to the +V state. Organic substances in the feedwater can foul the resin and decrease its capacity for arsenic removal. Such organic material must be removed by pretreatment with activated carbon or other techniques (Wachinski and Etzel, 1997).

An important parameter to determine the feasibility of using the ion exchange process for arsenic removal is to determine the number of bed volumes (BV) which can be treated prior to arsenic breakthrough (a sharp rise in the arsenic concentration of the effluent). Bed volume is defined by the equation below:

$$BV = {V_B}/{V} \qquad \text{Equation 8}$$

where:

BV = number of bed volumes treated
V_B = the volume of water treated, ft^3
V = the bulk volume of resin or media in the contactor, ft^3

Chen *et al.* (1999) reported an estimation of the bed volumes treated before 10% arsenic breakthrough with anion exchange based on the influent sulfate levels as given in the equations below:

$$BV_{AX} = -606 \cdot \mathrm{Ln}(C_{SO4}) + 3{,}150 \qquad \text{for } SO_4^{2-} < 120 \text{ mg/L} \qquad \text{Equation 9}$$

$$BV_{AX} = -200 \cdot \mathrm{Ln}(C_{SO4}) + 1{,}250 \qquad \text{for } SO_4^{2-} > 120 \text{ mg/L} \qquad \text{Equation 10}$$

where:

BV_{AX} = number of bed volumes treated using anion exchange before 10% As breakthrough
(C_{SO4}) = initial sulfate concentration, mg/L

These equations were developed using best-fit trendlines to model predictions.

The following example calculation illustrates the use of the above equations:

Given: Anion exchange plant

Influent SO_4^{2-} = 30 mg/L

Influent As = 30 µg/L

Required: The number of bed volumes treated before 10% breakthrough of arsenic

Solution: $BV_{AX} = -606 \cdot \mathrm{Ln}(C_{SO4}) + 3{,}150$

$BV_{AX} = -606 \cdot \mathrm{Ln}(30\ \mathrm{mg/L}) + 3{,}150$

BV_{AX} = 1,090 Bed Volumes

Clifford (1999) identified nine important factors to consider when designing an ion exchange system for drinking water treatment:

(1) choice of SBA resin,

(2) effect of multiple contaminants such as arsenic and nitrate,

(3) arsenic leakage,

(4) effect of sulfate concentration,

(5) optimum empty bed contact time (EBCT),

(6) regenerant strength (% NaCl),

(7) regenerant level (lbs NaCl/ft^3 resin),

(8) spent-brine reuse, and

(9) spent-brine treatment

Studies conducted by EPA (2000f) of two existing small-scale ion exchange drinking water systems, showed that the process consistently achieved levels of arsenic < 5 µg/L when the resin was properly regenerated. Removal efficiencies in their study were 53% and 97% for arsenic. One plant achieved lower removal efficiencies due to insufficient regeneration and also because of chromatographic peaking due to sulfate competition. Fox and Sorg (1987, 1989) with EPA, studied several POU ion exchange

systems in Alaska and Oregon. The systems were capable of lowering arsenic levels to less than 5 μg/L in a majority of samples, with influent concentrations ranging from 100 to 1,160 μg/L. Pilot-plant tests conducted by Clifford and his coworkers (1999) at McFarland, CA, Hanford, CA, and Albuquerque, NM, showed that ion exchange could treat to a level of 2 μg/L when treating a 10 to 50 μg/L arsenic contaminated groundwater containing up to 220 mg/L sulfate.

2.5.5 Activated Alumina

Activated alumina adsorption is a physical/chemical process by which ions in solution are removed by the available adsorption sites on an oxide surface. Activated alumina is a semicrystalline porous inorganic adsorbent. It has a higher zero-point-of-charge (zpc) (pH_{zpc}=8.2) than most oxide minerals, thus causing it to have an affinity for many anions in water with near-neutral pH. The adsorption process involves surface complexation and exchange of hydroxide ions (OH^-) for the contaminants (Chwirka *et al.*, 2000). The typical activated alumina used in water treatment processes are 28- X 48-mesh (0.3- to 0.6-mm diameter) mixtures of amorphous and gamma aluminum oxide (γ-Al_2O_3) prepared by low-temperature (300 to 600^{0}C) dehydration of precipitated $Al(OH)_3$. The result is a highly porous material with surface areas of 50 to 300 m^2/g (Clifford, 1999). A typical activated alumina process diagram is shown in Figure 10.

This process is considered favorable to ion exchange for arsenic removal primarily because of the selectivity sequence for alumina. Alumina has a very high affinity for arsenic and fluoride ions over other traditional competing ions such as sulfate, carbonate, and chloride in contrast to the selectivity for anion exchange resins. Clifford

(1999) reports the selectivity sequence for activated alumina in the pH range of 5.5 to 8.5 as the following:

$$OH^- > H_2AsO_4^-, Si(OH)_3O^- > F^- > HSeO_3^- > SO_4^{2-} > CrO_4^{2-} >> HCO_3^- > Cl^- > NO_3^- > Br^- > I^- \quad \text{Equation 11}$$

Sulfate offers only a very minor competition for sorption sites with activated alumina whereas with ion exchange, it can be a significant problem.

The feedwater pH is more critical to arsenic removal by activated alumina adsorption than any other process. The pH of the feedwater must be sufficiently lower than the pH_{zpc} so that the activated alumina media has a high density of positively charged sites (Chwirka *et al*., 2000). Below this pH, the activated alumina surface has a net positive charge which can be balanced by adsorbing anions like arsenate. Various studies have shown that the optimum pH is in the range of 5.5 to 6.0, with optimum being closer to 6.0, for arsenic removal (U.S. EPA, 2000f; Clifford, 1999; Fox, 1989).

Clifford (1999) proposed that a model for process design of activated alumina is analogous to a weak base anion exchange resin, which only operates effectively in the acidic pH range. First, the alumina surface must be protonated to begin the removal of $H_2AsO_4^-$ from solution. This is accomplished by preacidification with HCl or H_2SO_4 and reducing the feedwater pH into the 5.5-6.0 region. The step of alumina acidification can be written as the following where again the bar indicates a solid or surface phase:

$$\overline{\text{Alumina} \cdot \text{HOH}} + \text{HCl} \Rightarrow \overline{\text{Alumina} \cdot \text{HCl}} + \text{HOH} \quad \text{Equation 12}$$

The next step is the service of the column in which the HCl-acidified alumina is contacted with the arsenate ions, displacing the chloride ions in a fashion similar to anion exchange. This step can be written as follows:

$$\overline{\text{Alumina} \cdot \text{HCl}} + \text{H}_2\text{AsO}_4^- \Rightarrow \overline{\text{Alumina} \cdot \text{H}_2\text{AsO}_4} + \text{HCl} \qquad \text{Equation 13}$$

Once the sorptive capacity of the alumina has been reached, the media must be regenerated. This can be accomplished by using a solution of NaOH (up to 4% may be required) which displaces the arsenate from the alumina as follows:

$$\overline{\text{Alumina} \cdot \text{H}_2\text{AsO}_4} + \text{NaOH} \Rightarrow \overline{\text{Alumina} \cdot \text{HOH}} + \text{NaHAsO}_4 \qquad \text{Equation 14}$$

To restore the arsenic removal capacity to the alumina, the media must then be acidified again by contacting it with 0.5 N HCl or H_2SO_4 as discussed above.

With the benefit of the high selectivity for arsenic of the activated alumina, there is a drawback in that the anions are very difficult to remove from the media during regeneration. Due to this, typically only 75% of the adsorbed arsenic is recovered from the alumina during regeneration, which results in deterioration of adsorptive capacity over time (Clifford, 1999).

As with ion exchange, activated alumina is considerably more effective at removing As(V) than As(III). Therefore, if As(III) is found to be present in the feedwater, prechlorination or some other means of oxidation prior to the alumina column

will be necessary. Prefiltration will also be necessary to prevent clogging and fouling of the media by suspended solids and particulate iron in the feedwater if their levels are significantly high.

Factors listed by Clifford (1999), Frey *et al*. (1998), and U.S. EPA (2000f) which significantly affect the design process for activated alumina arsenic removal are:

(1) arsenic species in feedwater,

(2) pH of feedwater,

(3) competing anions,

(4) empty bed contact time (EBCT),

(5) regeneration or throw-away of media,

(6) concentration of arsenic in feedwater (higher concentrations lead to shorter run length), and

(7) alumina particle size (finer particles of alumina have higher arsenic capacity, lower arsenic leakage, and longer run length than larger particles).

Activated alumina processes have much longer run times (time between regenerations of media) for arsenic removal than do ion exchange processes, thus making the process amenable to use on a media throw-away basis. Operating in this fashion would prevent small plant operators from having to use hazardous chemicals such as sodium hydroxide and sulfuric acid to regenerate the media. An important parameter to determine the feasibility of using activated alumina for arsenic removal is to determine the number of bed volumes which can be treated prior to arsenic breakthrough. Chen *et al.* (1999) reported an estimation of the bed volumes treated before 10% arsenic

breakthrough with activated alumina. Unlike the ion exchange model given previously where run lengths were affected by influent sulfate levels, the activated alumina model is based primarily on influent arsenic concentrations as given in the equation below:

$$BV_{AA} = 2.1\times10^{5} \cdot (As)^{-0.57} \qquad \text{Equation 15}$$

where:

BV_{AA} = number of bed volumes treated using activated alumina before 10% As breakthrough

(As) = initial arsenic concentration in μg/L

This equation was also developed using best-fit trendlines to model predictions.

The following example calculation illustrates the use of the above equations:

Given: AA adsorption plant

Influent As = 30 μg/L

Required: The number of bed volumes treated before 10% breakthrough of arsenic

Solution: $BV_{AA} = 2.1\times10^{5} \cdot (As)^{-0.57}$

$BV_{AA} = 2.1\times10^{5} \cdot (30\,\mu g/L)^{-0.57}$

BV_{AA} = 30,200 bed volumes

Activated alumina has effectively removed arsenic in pilot studies and in POU applications (Frey *et al*., 1998). Studies by the EPA (2000f) of existing small-scale

alumina facilities in the New England area showed that the process was capable of treating to levels of 5 μg/L or less with influent concentrations from 34 to 87 μg/L arsenic. Average arsenic removal efficiencies for these plants were 87% and 98%. Sorg and Logsdon (1978) cited alumina studies done by Bellack in 1970, which showed a decrease in arsenic from 60 μg/L to 3 μg/L, and by Rubel and Alcoa Laboratories in 1977 which showed a decrease in arsenic from 1,000 μg/L to below 5 μg/L. Pilot-plant studies by Hathaway and Rubel (1987) found extended runs (8542 bed volumes of treated water) were possible with activated alumina and pH adjustment to 5.5. Effluent concentrations of arsenic were reduced from a range of 80-116 μg/L to less than 5 μg/L. Fox and Sorg (1987) and Fox (1989) found using POU devices in Alaska and Oregon, that activated alumina was capable of reducing arsenic concentrations from a range of 50-1,160 μg/L in the feedwater to effluent levels below 5 μg/L.

2.5.6 Membrane Separation Processes

Membrane processes can be defined as technologies that use a barrier to the flow of suspended, colloidal, or dissolved species in any solvent. Membrane processes with the greatest immediate application to potable water treatment are reverse osmosis (RO), nanofiltration (NF), electrodialysis reversal (EDR), ultrafiltration (UF), and microfiltration (MF) (Taylor and Wiesner, 1999). These processes are grouped according to their pore sizes and particle removal ranges as depicted in Figure 11. From the figure it is evident that RO, EDR, and NF technologies should be able to remove contaminants in the ionic range such as arsenic. The EPA (2000d) lists only reverse osmosis and electrodialysis reversal as BATs in their proposed regulation for the new arsenic MCL.

NF was not included as a BAT because, when operated at realistic recoveries, the removal efficiency of arsenic is low. EDR was also not thought to be as competitive with RO on costs and removal efficiencies (U.S. EPA, 2000d). Therefore the focus of this section will be on RO membranes with some discussion of EDR processes. A typical process diagram using membrane filtration is shown in Figure 12.

Membrane processes are generally classified according to the driving force used to transport the contaminants from solution. The driving forces can include pressure, concentration, electrical potential, and temperature. RO and NF membranes are pressure driven processes requiring a certain amount of pressure to transport the feedwater across the membrane. Of the membranes mentioned earlier, RO have the smallest minimum pore size thus requiring the greatest amount of driving pressure and also resulting in the least recovery. Solute mass transport is said to be diffusion and size exclusion controlled in RO and NF, unlike MF and UF systems which are only controlled by size exclusion (Taylor and Wiesner, 1999). Typical pressure ranges for NF membranes are 50-150 psi. The typical range for RO membranes is 100-150 psi (U.S. EPA, 1999). An RO membrane rejects solutes as small as 0.0001 μm, which is in the ionic or molecular size range. An NF membrane rejects solutes as small as 0.001 μm, which is also in the ionic or molecular size range (Taylor and Wiesner, 1999).

EDR systems are not pressure driven and do not rely on the pore size for contaminant removal. Rather they rely on charge for solute separation from the feedwater. They pass the solute through the membrane rather than the solvent or the feedwater like RO systems. EDR membranes can be considered as porous sheets of ion exchange resin with a relatively low permeability for water (Taylor and Wiesner, 1999).

EDR processes can remove contaminant ions down to atomic sizes. Few tests have been conducted on EDR systems to evaluate their arsenic removal potential. One full-scale EDR plant in Buckeye, AZ installed primarily for the removal of high TDS, showed an average arsenic removal of 69.4% (reduction from 66 to 20 μg/L) (Ionics, Inc., 2000).

There are several terms to be familiar with when evaluating membrane technologies because of their seldom use with regard to other common water treatment technologies. Table 8, portions of which are from Taylor and Wiesner (1999), defines several of the terms frequently used. Two terms commonly used to define membrane effectiveness are recovery and rejection. Recovery is defined as the percentage of feedwater that can be converted to product water and is calculated by the equation below:

$$\text{Recovery}\ (\%) = 100 \cdot \frac{Q_p}{Q_f} \qquad \text{Equation 16}$$

where:

Q_p = Product or permeate flow, gpd
Q_f = Feedwater flow, gpd

Rejection is defined as the percentage of contaminant removed, which in this case would be arsenic, and can be calculated by the following equation:

$$\text{Rejection}\ (\%) = 100 \cdot \left(1 - \frac{C_p}{C_f}\right) \qquad \text{Equation 17}$$

where:

C_p = Concentration of contaminant in product or permeate water, µg/L

C_f = Concentration of contaminant in feedwater, µg/L

Rearranging Equations 14 and 15, one can find the concentration of a pollutant in the permeate, C_p, given the pollutant rejection and the concentration of the pollutant in the concentrate stream, C_c with the following equations:

$$C_p = (1 - \text{Rejection})(C_f) \qquad \text{Equation 18}$$

where:

C_p = Concentration of pollutant in the permeate
C_f = Concentration of pollutant in the feed water
Rejection = Decimal fraction rejection of pollutant

$$C_c = \frac{Q_f C_f - Q_p C_p}{Q_c} \qquad \text{Equation 19}$$

where:

C_c = Concentration of pollutant in concentrate water

Q_c = Concentrate water flow

The following example calculation illustrates the use of Equations 14 through 17:

Given: Membrane plant producing 1-mgd (Q_p) with 75% recovery

95% rejection of arsenic

Influent As = 30 µg/L

Required: Concentrate flow

Arsenic concentrations in permeate and concentrate

Solution:

$$Q_c = \frac{Q_p(1-\text{Recovery})}{\text{Recovery}} = \frac{1\,\text{mgd}(1-0.75)}{0.75} = 0.333\,\text{mgd}$$

$$C_p = (1-\text{Rejection})(C_f) = (1-0.95)(30\,\mu\text{g/L As}) = 1.5\,\mu\text{g/L As}$$

$$C_c = \frac{Q_f C_f - Q_p C_p}{Q_c} = \frac{1.333\,\text{mgd}(30\,\mu\text{g/L}) - (1\,\text{mgd})(1.5\,\mu\text{g/L})}{0.333\,\text{mgd}} = 116\,\mu\text{g/L As}$$

Waypa *et al*. (1997) conducted bench-scale experiments on arsenic removal using RO and NF membranes. They concluded:

- High removal efficiencies of As(III) – comparable to those of As(V) – were obtained using RO and tight NF membranes. This is explained by the relatively large molecular weight of arsenic species (126 g/mole for H_3AsO_3 and 140 g/mole for $HAsO_4^{2-}$) which controls their separation by the membrane and not the charge of the species. Therefore these membranes seem most suitable for As removal from groundwater in which most of the arsenic is in the As(III) form. This also eliminates the need for preoxidation, which is detrimental to the performance of thin-film composite membranes.
- Applied pressure had little effect on arsenic removal, but an increase in feedwater temperature (over the range of 15-30^{o}C) decreased arsenic removal by a small percentage.
- Removal of arsenic by the membranes used was independent of pH (in the range of 4 to 8 that was tested), thus eliminating the need for pH optimization.

- Dissolved co-occurring inorganic solutes did not affect arsenic rejection by RO and NF membranes. Therefore, RO and NF membranes should be effective for a variety of source water qualities. However, the possibility of precipitation of sparingly soluble inorganic salts should be considered at high recoveries.
- Long-term membrane performance and possible deterioration in performance over time because of colloidal and NOM fouling should be considered. Pretreatment of surface water may be needed to prevent fouling. Levels of colloids and NOM are usually low in groundwaters, thus no pretreatment may be required.
- Arsenic rejection may be reduced at high recoveries because of concentration polarization and membrane fouling.

Membrane fouling is an important consideration in the design and operation of a membrane system. Fouling is a reduction in the permeate flux due to the accumulation of materials on, in, or near the membrane. Taylor and Wiesner (1999) identified three fouling mechanisms which act to reduce the flux in membrane processes:

- Concentration polarization: Contaminants rejected by the membrane tend to concentrate at the membrane surface and "back-diffuse" away from the membrane surface thus reducing the flux across the membrane.
- Precipitative fouling: The elevated concentrations of contaminant ions at the surface of RO and NF membranes results in the potential for precipitation of various minerals on the membrane surface, resulting in fouling.
- Clogging by cake (or gel) formation: Solids deposition on the membrane surface can result in formation of a cake and compaction of the membrane that represents an additional mass transfer resistance. Flushing or backwashing the membrane

module is capable of reversing much of this fouling. Gel layers of deposited NOM can also form and are generally more difficult to reverse.

Cleaning frequency, pretreatment requirements, operating conditions, cost, and performance are affected by membrane fouling (Taylor and Wiesner, 1999). The smaller pore size of NF and RO membranes makes them more prone to fouling than UF and MF membranes. The rejection of scale-causing ions like calcium can lead to precipitation on the membrane surface. Organic compounds and metal compounds like iron and manganese can promote fouling. Precipitation must be avoided by appropriate pretreatment including addition of anti-scaling chemical and/or acid to the feedwater (U.S. EPA, 1999).

Estimates of water production and water quality for various parameters when using RO membrane systems can be found by using manufacturer computer programs. Dow-Filmtec, Hydranautics, Fluid System, and TriSep are examples of manufacturers which provide computer programs for the design of RO plants. A number of these can be found and downloaded on the World Wide Web (WWW). Typical input parameters for the programs are feedwater rate, TDS concentration, feed temperature, recovery, array type, number of elements in pressure vessel, and element type. The programs do not give complete designs, however they can serve as a tool for developing and testing various membrane system configurations (Taylor and Wiesner, 1999).

Most conventional RO and NF treatment systems also will include pretreatment and post-treatment units. RO performance can be adversely affected by the presence of turbidity, iron, manganese, silica, scale-producing compounds and other constituents (U.S. EPA, 1999). Pretreatment processes might include antiscalant and/or acid addition,

cartridge microfiltration, GAC filtration, or aeration depending upon the quality of the feedwater. Post-treatment processes that might be used are operations common to drinking water treatment such as disinfection, aeration, and corrosion control (Taylor and Wiesner, 1999).

Several pilot-plant and field tests have been conducted to determine the feasibility of using RO and NF membranes for arsenic removal. EPA funded the installation of 73 RO POU treatment systems in San Ysidro, N.M. in the mid 1980's. Raw water arsenic levels ranged from 68 to 230 μg/L. The RO units were able to reduce the arsenic levels to a range from < 5 μg/L to 20 μg/L with 20-30% recovery (Fox and Sorg, 1987). The bench-scale experiments conducted by Waypa *et al*. (1997) concluded that 94.5-100% arsenic removal could be achieved with thin-filmed composite RO membranes. Tests on NF membranes by the AWWARF showed high As(V) rejection (~95%) while As(III) rejection averaged only 40% presumably due to the influences of diffusion and electrostatic repulsion (U.S. EPA, 1999). AWWARF pilot-scale tests on RO membranes achieved > 95% rejection of As(V) while rejection of As(III) averaged only 74% (U.S. EPA, 1999). The AWWARF studies indicate the importance of preoxidation to As(V) if substantial amounts of As(III) are present in the feedwater.

2.5.7 Alternative and Innovative Adsorption Technologies

There are a number of other technologies discussed in the literature which are currently being investigated for arsenic removal. These include oxidation/greensand filtration, granular ferric hydroxide (GFH), sulfur modified iron (SMI), iron filings, and iron-coated activated alumina. These technologies have shown promise, however more

testing will be required before they can be considered for use in full-scale arsenic removal facilities. Some of these technologies will be discussed briefly in this section. Many of these media adsorption technologies can be grouped together and have a similar process scheme as shown in Figure 13.

Oxidation/greensand filtration is a process commonly used for iron and manganese removal in drinking water treatment. Greensand is a zeolite-type glauconite material which is produced by treating glauconite sand with $KMnO_4$ until the sand is coated with a layer of manganese oxides, particularly manganese dioxide (U.S. EPA, 1999). Potassium permanganate is fed either continuously or intermittently to the raw unaerated groundwater. Iron and manganese precipitates coat the greensand. The media has the ability to sorb any soluble iron and manganese and oxidize them on the media. When the exchange capacity is exhausted, the media is regenerated with a solution of excess $KMnO_4$ after backwash or when needed. Essentially, the greensand acts as a buffer to remove any iron and manganese not oxidized by the continuous permanganate feed (Robinson, 2000). Mechanisms of arsenic removal by this process include oxidation, ion exchange, and adsorption. Both the $KMnO_4$ feed and the oxidative nature of the manganese surface converts the As(III) to As(V). The As(V) can either displace species from the manganese oxide (presumably OH^- and H_2O) and become bound to the greensand surface or it can be adsorbed to the surface (U.S. EPA, 1999). Column tests by Bajpai and Chaudhuri (1999) with 500 µg/L As(III) and 500 µg/L As(V), achieved bed volumes of 153-185 per cycle at a breakthrough value of 10 µg/L. Driehaus *et al*. (1995), in bench-scale studies of As(III) oxidation with manganese dioxide coated sand filters, found that As(III) oxidation and adsorption was efficient and the release of soluble

manganese was low. The effectiveness of greensand filtration on arsenic removal has been shown to be highly dependent on the influent iron concentration, therefore EPA (2000d) has stated that it may only be appropriate with systems that do not require much arsenic removal and have high iron in their source water.

Granular ferric hydroxide (GFH) is an adsorbent process similar to activated alumina and is contained in fixed bed reactors. Driehaus et al. (1998) reported that the application of GFH in test adsorbers showed a high treatment capacity of 30,000 to 40,000 bed volumes until an arsenic limit of 10 μg/L was exceeded. As(V) adsorption decreased with pH and phosphate in the source water reduced arsenic removal due to competition. The most significant drawback to this process is the cost of the GFH media which is said to be approximately $4,000 per ton (U.S. EPA, 1999).

Sulfur modified iron (SMI) is a patented process by Hydrometrics, Inc., developed for arsenic removal. The process has three components: 1) finely-divided metallic iron, 2) powdered elemental sulfur, or other sulfur compounds, and 3) an oxidizing agent. The powdered iron, powdered sulfur, and the oxidizing agent are thoroughly mixed and then added to the water to be treated. The solution is then mixed and settled. Packed bed reactors and fluidized bed reactors may be used in SMI treatment systems (U.S. EPA, 1999; 2000d). The mechanism of arsenic removal with this process is adsorption. The process is currently being laboratory tested to develop design parameters for a pilot-scale system in a project sponsored by The Montana Water Center and investigated by University of Nevada – Reno, Hydrometrics, and others.

The process of iron filings and sand, originally developed for removal of arsenic at remediation sites, has also been considered for drinking water arsenic removal. At

present, there is no data available in the literature that indicates the process can remove arsenic at the low levels encountered in drinking water (U.S. EPA, 1999).

2.6 Disposal of Residuals

The disposal of residuals is very important for the design engineer of drinking water treatment systems to consider. Some residuals from arsenic treatment facilities may be considered hazardous waste and would have to be disposed of as such. Arsenic wastes are considered hazardous if their toxicity characteristic (TC) exceeds 5 mg/L of arsenic. The Toxicity Characteristic Leaching Procedure (TCLP) is used to determine if it exceeds the TC. If waste is < 0.5% dry-weight solids, then the liquid is defined as the TCLP extract and concentrations in it are compared against the TC level to determine if it is hazardous (U.S. EPA, 2001b). Also, costs of residuals disposal can be a significant portion of the total operating costs for some technologies. It is estimated that when enhancing existing processes such as coagulation/filtration and lime softening for arsenic removal, the residuals handling and disposal costs are as much as 80% and 88% of the total cost, respectively. With other technologies, residuals handling and disposal costs could be on average 12-34% of the total costs (Frey *et al*., 1998). Disposal alternatives for liquid waste streams include: direct discharge, indirect discharge, underground injection, and land disposal. Alternatives for solids/sludges include: land disposal, reuse, and incineration. Table 9 shows a summary of several treatment processes used for arsenic removal, the various residuals produced, and possible disposal methods for the residuals. The following section gives an overview of the various residuals produced from each technology and their possible treatment and disposal methods.

2.6.1 Conventional Treatment Processes

Conventional treatment processes such as coagulation/filtration, lime softening, and iron and manganese removal will also generate residuals that must be disposed of. The residuals from these processes will primarily be settled sludges and filter backwash water. The quantities of sludge produced will increase with the increased coagulant dosage used to remove arsenic. Filter backwash water will contain levels of arsenic dependent upon the influent concentrations and amount removed. The levels of arsenic present in the backwash will have to be considered when evaluating a disposal option, whether it be discharged directly to rivers, discharged indirectly to wastewater treatment plants, or recycled within the water treatment plant (Chen *et al*., 1999).

2.6.2 Ion Exchange Processes

Ion exchange processes produce residuals primarily from regeneration of the media. Waste streams will include backwash water, regenerant brine solution, and rinse water. These streams consist of 1.5 to 10% of the treated water volume depending on the feedwater quality and the type of ion exchange unit (U.S. EPA, 2000a). The regenerant solution used is usually sodium chloride. According to Albuquerque field study results (Clifford, 1999), spent brine could possibly be reused at least 20 times, thus reducing the quantity of waste residual. Once wasted, the arsenic can be precipitated out of the spent brine solution using Fe(III) or Al(III) salts with the precipitate expected to be non-hazardous (TCLP for As < 5.0 mg/L) (Clifford, 1999; Chwirka *et al*., 2000). The problem of disposing of a high TDS regenerant waste must be considered when using ion

exchange processes. Few POTWs will be able to accept high TDS discharges, thus ion exchange will have limited use for arsenic removal except where sulfate levels are low (≤ 50 mg/L) and the brine volume is very small compared to the total volume at the POTW (U.S. EPA, 2001b).

2.6.3 Activated Alumina Processes

Activated alumina systems produce regenerant waste streams and when operated on a throwaway media basis, spent alumina. Regenerant streams consist of backwash water, regenerant (caustic), neutralization stream (acidic), and rinse waters. Accumulated arsenic and dissolved aluminum in the waste caustic solution can be treated in a batch process by neutralizing with H_2SO_4 (or HCl) and precipitating $Al(OH)_3$ (Clifford, 1999; Chwirka *et al*., 2000). The dewatered sludge is expected to be non-hazardous. Spent alumina would probably pass the TCLP and EP toxicity tests due to the arsenic loading being very low and the tests are performed at pH 5, which is near the optimum pH for arsenic adsorption on alumina (Clifford, 1999). In the final rule, EPA (2001b) did not recommend regeneration of activated alumina media due to a number of reasons, including the difficulty in disposing of the brines.

2.6.4 Membrane Processes

Membrane processes produce a concentrate stream (reject water stream) which will contain the rejected arsenic and other substances which are rejected by the membrane. The concentrate stream is generally high in TDS and the quality of the concentrate will vary depending upon the level of arsenic and other contaminants in the

feedwater. Disposal of the high TDS brines from membrane processes will also be difficult to dispose of unless local POTWs and their treatment processes are compatible with this waste. Taylor and Wiesner (1999) listed surface discharge as the most common concentrate disposal practiced and sewer discharge the second most common for small plants.

2.7 Cost Data for Treatment Technologies

The new MCL for arsenic is expected to have a total annualized cost of approximately $181 million (U.S. EPA, 2001b). Much of this cost will be for the installation of new treatment trains to meet the MCL. Under contract with EPA, International Consultants, Inc., Malcolm Pirnie, Inc., and The Cadmus Group, Inc., developed the *Technologies and Costs for Removal of Arsenic From Drinking Water* document (U.S. EPA, 2001a) which presents capital and O&M cost curves for numerous arsenic removal technologies. Table 10 gives a comparison of the costs for 0.01-, 0.1-, and 1-MGD average flow facilities using the technologies indicated. Costs given for enhanced coagulation and enhanced lime softening are only for enhancements to an existing facility. Figures 14, 16, and 18 show graphical comparisons of the capital costs of the various treatment technologies. Figures 15, 17, and 19 show graphical comparisons of the O&M costs of the technologies.

CHAPTER 3

METHODS AND MATERIALS OF MULTIMEDIA CD-ROM PRODUCTION

3.1 CD-ROM Development Approach

The intent of this project was to development a program which can be distributed by CD-ROM as an executable file. Macromedia Authorware® version 5 was used as the authoring tool to develop the CD-ROM piece. The software is capable of producing CD-ROM and Web-based presentations with rich multimedia components such as digital videos, digital photos, sounds, and interactive text. The program is packaged with only a runtime version of Authorware therefore, the end-user of the presentation will not have the ability to edit any of the final product. The final distributed copy of the program is an executable (.exe) file on the CD-ROM and does not require any special programs to run from an end-user's personal computer.

3.2 Pilot-Plant Site Visits

A major portion of this project was the need to acquire photos and video of existing arsenic removal plants to incorporate into the presentation. Contacts were made by telephone and e-mail to EPA and various state and local environmental agencies to locate existing arsenic removal facilities in the United States. There are relatively few arsenic treatment facilities in the U.S. and these facilities are generally small and were designed for an MCL of 50 μg/L. The majority of existing facilities that were located were non-transient, non-community type systems in place at locations such as schools

and industries. The result of this search was the discovery of several pilot-plant facilities for large municipalities located in Phoenix and Tucson, Arizona.

The Phoenix pilot-plant site was visited on January 29, 2001. The pilot-plant facility was set up at the Phoenix Water Services Well #280. Existing treatment at the well consisted only of chlorination prior to distribution. Arsenic levels at this well are typically around 17 μg/L. The pilot-scale facilities included the testing of two skids with four adsorbents in 1-ft diameter columns. The processes were set up in 4 parallel treatment trains. Flow rates for the processes were 3-5 gpm to each column. The four adsorbents included in the testing were granular ferric hydroxide, Alcan FS-50 (iron-coated activated alumina), activated alumina, and Apyron Aquabind. Previous bench-scale testing of 20 adsorbents in Phoenix narrowed down adsorbent media to the best four that were in use at the site. The contact for the Phoenix test facility was Ramesh Narasimhan, P.E. of NCS Consulting Services, Phoenix, Arizona.

The Tucson pilot-plant site was visited on January 30, 2001. The pilot-plant facility was set up at Tucson Water's Well #SC16 and all of the pilot-plants withdrew water from the well water prior to distribution. The only existing treatment at the well is chlorination. Raw water arsenic concentrations typically range from 15 – 20 μg/L and sulfate concentrations range from 110 – 120 mg/L. Pilot-scale facilities in place were adsorbent columns (4 adsorbents), anion exchange, Kinetico's coagulation-assisted Macrolite^{TM} ceramic media filtration, and Kruger's Metclean^{TM} fluidized-bed reactor process. A fifth pilot-plant consisting of coagulation and microfiltration units was under construction at the time of the visit. Flow rates for the processes ranged from 5 to 20

gpm. The contact for the Tucson test facility was Sunil Kommineni, Ph.D., P.E. of Malcolm Pirnie, Inc. in Tucson, Arizona.

3.3 Data File Preparation

Pictures were taken with a digital camera and a 35mm camera (primarily as a back-up) and video was taken with a standard Hi8 camcorder while at each of the project sites. Upon return, it was necessary to get all of this data into a format that was compatible for use in Authorware. For the pictures, for educational purposes, it was necessary to add informative text and titles to each picture (approximately 80 pictures were used in the presentations). The analog movie files were digitized and informative text and titles were added as well. The approximately 25 movie files, once edited, ranged in length from 7 seconds to 3 minutes and 53 seconds, and file sizes ranged from 1.4 to 42 megabytes. The following sections provide more detail on the procedures that were used to ready the photos and video for use in the presentation.

3.3.1 Photo & Slide Preparation Procedure

The equipment used for taking photos and slides at the various facilities and preparing them for use in the CD-ROM is as follows:

- Canon AE-1 35mm camera
- Olympus Camedia digital camera (1.3 megapixel)
- Kodak 35mm ISO 200 film for color slides
- HP slide scanner
- Microsoft® Photodraw™ 2000

For consistency amongst all of the photos and slides used in the CD-ROM, the following procedure was followed:

- Download the digital photos from the Olympus camera
- Scan the developed 35mm slides using HP slide scanner (add brightness/darkness and color as needed before saving file)
- Add title and text to photos using MS Photodraw (title font size = 18, descriptive text font size = 12, background color = R-254, G-255, B-166)

Once completed, all of the photos and slides must be the proper size to fit into the 640 X 480 pixels presentation screen in Authorware. The type of photo (digital vs. slide) dictated different procedures for resizing the final photos with text. The procedures are outlined below:

- Original pictures were 1280 X 960 pixels (digital) and 900 X 600 pixels (slides)
- Using PhotoDraw, pictures were resized to 1110 X 835 pixels (digital) and 617 X 412 pixels (slides)
- Vertical shots that were taken with the cameras must be set to a smaller size to allow for the whole picture to be viewed in Authorware; these settings were 650 X 870 pixels (digital) and 285 X 482 pixels (slides)
- If text was incorporated into the photo using PhotoDraw prior to the resizing, the picture and text must first be grouped and then the picture can be dragged to the appropriate size
- All pictures were saved as .jpg files for use in Authorware each having a file size of about 45 kilobytes; approximately 80 pictures were incorporated into the presentations

3.3.2 Movie File Preparation Procedure

The equipment used for filming video clips at the various facilities and preparing the clips for use in the CD-ROM is as follows:

- Sony video Hi8 Handycam CCD-TR600
- Sony Hi8 video cassettes
- Standard tripod
- Gateway™ 433c computer
- Dazzle* Digital Video Creator
- Adobe® Premiere® 5.0
- Ulead® Video Studio™ Version 3.0

MPEG (Motion Pictures Expert Group) format was chosen as the standard movie file format throughout the CD-ROM due to its ability to be played back without any special hardware on virtually all of the PCs available today and its relatively small file size. MPEG is a video compression-decompression (CODEC) software. A CODEC is necessary to produce reasonably sized video files. Without a CODEC, the file size required for 1 minute of video on a 640 x 480 viewing area is approximately:

$$\text{File size} = \left(\frac{640 \times 480 \text{ screen bits}}{\text{frame}}\right) \cdot \left(\frac{24 \text{bits color}}{1 \text{ screen bit}}\right) \cdot \left(\frac{24 \text{ frames}}{\text{sec}}\right) \cdot \left(\frac{60 \text{ sec}}{\text{min}}\right) \cdot \left(\frac{1 \text{ byte}}{8 \text{ bits}}\right)$$

$$= 1{,}327{,}000{,}000 \text{ bytes (or } 1.327 \text{ GB)}.$$

The data transfer rate would be about 22,000,000 bytes/sec. Both the file size and data transfer rate are beyond the capabilities of PC's. CODECs reduce the file size by several techniques such as averaging several pixels together, reducing the number of colors, only coding differences from one frame to the next, etc. Once compressed, typical one minute video file sizes for this presentation were around 11,500,000 bytes and data rates were approximately 150-200 kilobytes/sec. For consistency amongst all of the video files in the CD-ROM, the following procedure was followed in preparing the video clips:

- Digitize the video clips using Dazzle* DVC resulting in a .mpg file
- Using Adobe Premiere edit video clips to desired length
- Using Adobe Premiere add titles and text to video clips (text settings: font size titles = 18, font size descriptive text = 14, color R-221, G-255, B-22)
- Export project from Adobe Premiere resulting in a .mov file (export settings: size 320 x 240, 29.97 fps, Intel Indeo Video 4.4 codec)
- Using Ulead software, convert .mov file to final .mpg file for use in Authorware

3.4 Authorware Screen Production

The "multimedia piece" that was developed for this project contained media objects such as digital video, photos, example plans, graphics, and text, among other items. The common trait in a multimedia piece is the ability to orchestrate these objects in response to changing conditions such as a user's choices. The assembling of multimedia into a functioning piece is known as authoring (Macromedia, Inc., 1998). The authoring technique used in Authorware is referred to as "icon-based" authoring. Media types are assembled within specific icons and placed on a flowline. The flowline determines the sequence in which the program runs.

To be consistent with previous pieces which were completed by Dr. Bruce Robinson, the Slow Sand Filtration and Iron and Manganese Control pieces, the format of the Arsenic Removal piece generally follows the same format. The general appearance such as the text styles and colors and the navigational buttons which appear at the bottom of the screen do not change from Dr. Robinson's work to the Arsenic Removal work.

The major content headings used in the piece were suggested by Dr. Robin Collins of the University of New Hampshire at a Conference on Small Water Treatment Technologies. They are intended to provide a standard reporting format for research involving small water treatment technologies and to insure that needed topics were covered for engineers involved in the design of these systems. Some of the general contents headings were not used, such as automation, due to the inapplicability with the arsenic removal presentation. Other headings were added to the piece, such as residuals, which were deemed important to the topic.

Once all of the data was collected and literature was reviewed for this project, it was necessary to develop a rough outline of how the final piece was going to be organized to encompass all of the data. This was done in PowerPoint by developing a storyboard, or rough graphical outline of the presentation with design notes on the screens to aid in the development process. The final presentation differed considerably from the original storyboard, however it was a useful tool to help organize the mass of information that went into the presentation. The original storyboard is included as Appendix E.

Figure 20 shows a flow chart of the navigational structure of the final arsenic module. Sample Authorware program screens from the arsenic module are provided as Appendix F. Most of the structure is set up in a linear fashion and can be simply navigated by clicking the "next" button on the screen. However, many of the pages on the main structure have link buttons which will take the user off the main path to charts, figures, curves, etc. Also, a hypertext table of contents is provided on the left side of the page so that the user can navigate directly to any section that may be of interest. Screen captures of the first page of each main section in the module are provided in Appendix G. The final arsenic module is provided on the accompanying CD-ROM and can be viewed by opening the file entitled "arsenic_watertech_cd.exe".

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APPENDICES

APPENDIX A

TABLES DISCUSSED IN BODY OF REPORT

Table 1. Cancer Risks for U.S. Populations Exposed at or Above MCL Options, After Treatment (Source: U.S. EPA, 2001b)

MCL (mg/L)	*Mean exposed population risk*	*90^{th} percentile exposed population risk*
3	$0.11 – 1.25 \times 10^{-4}$	$0.22 – 2.42 \times 10^{-4}$
5	$0.27 – 2.02 \times 10^{-4}$	$0.55 – 3.9 \times 10^{-4}$
10	$0.63 – 2.99 \times 10^{-4}$	$1.32 – 6.09 \times 10^{-4}$
20	$1.1 – 3.85 \times 10^{-4}$	$2.47 – 8.37 \times 10^{-4}$

Table 2. Principle Reactions Affecting Inorganic Arsenic Concentrations in Groundwater (Source: Welch et al., 2000)

Redox Condition	*Important Phases*	*Important Reactions*	*Conditions Affecting Mobility*
Oxic (oxygen)	Fe-oxides	Adsorption/desorption	pH; competing adsorbents; oxygen and iron concentrations
		Precipitation	
	Sulfide minerals	Sulfide oxidation	pH and microbial activity; oxygen and nitrate transport
Anoxic (no oxygen)	Fe-oxides	Adsorption/desorption and precipitation	Oxidation state of As
		Adsorption/desorption	pH
		Dissolution	Presence of organic carbon
	Sulfide minerals	Sulfide oxidation	
Sulfidic (sulfide present)	Sulfide minerals	Precipitation	Sulfide, iron, and As concentrations

Table 3. Comparison of National Arsenic Occurrence Estimates (Source: U.S. EPA, 2001b)

Source	*Type of water*	*System types*	*Population served*	*% of systems with mean arsenic exceeding concentrations (mg/L) of:*				
				2	3	5	10	20
Ground Water Systems								
EPA-proposed	Raw+finished	CWS	All	27.2	19.9	12.1	5.4	2.1
EPA-final	Raw+finished	CWS	All	27.3	19.9	12.1	5.3	2.0
NAOS-small	Finished	PWS	≤10,000	23.5	NR	12.7	5.1	NR
NAOS-large	Finished	PWS	>10,000	28.8	NR	15.4	6.7	NR
NIRS	Finished	CWS	All	17.4	11.9	6.9	2.9	1.1
USGS	Raw	PWS	All	25.0	NR	13.6	7.6	3.1
Surface Water Systems								
EPA-proposed	Finished	CWS	All	9.9	6.0	2.9	0.8	0.3
EPA-final	Finished	CWS	All	9.8	5.6	3.0	0.8	0.3
NAOS-small	Finished	PWS	≤10,000	6.2	NR	1.8	0.0	NR
NAOS-large	Finished	PWS	>10,000	7.5	NR	1.3	0.6	NR

Table 4. Best Available Technologies and Removal Rates (Source: U.S. EPA, 2001b)

Treatment technology	*Maximum percent removal [for As(V)]*
Ion Exchange (sulfate ≤ 50 mg/L)	95
Activated Alumina	95
Reverse Osmosis	>95
Modified Coagulation/Filtration	95
Modified Lime Softening (pH > 10.5)	90
Electrodialysis Reversal	85
Oxidation/Filtration (20:1 iron:arsenic)	80

Table 5. Small System Compliance Technologies for Arsenic (V) (Source: U.S. EPA, 2001b)

Treatment Technology	*Affordable for listed small system categories*
Activated Alumina (centralized)	All size categories
Activated Alumina (POU)	All size categories
Coagulation/Filtration	501-3,300 and 3,301-10,000
Coagulation/Microfiltration	501-3,300 and 3,301-10,000
Electrodialysis Reversal	501-3,300 and 3,301-10,000
Enhanced Coagulation/Filtration	All size categories
Enhanced Lime Softening (pH>10.5)	All size categories
Ion Exchange	All size categories
Lime Softening	501-3,300 and 3,301-10,000
Oxidation/Filtration (Fe/As ratio 20:1)	All size categories
Reverse Osmosis (centralized)	501-3,300 and 3,301-10,000
Reverse Osmosis (POU)	All size categories

Table 6. Summary of Reported Performance of Arsenic Removal Technologies in the Literature

Treatment Technology	*Type*	*Operating Parameters*	*Arsenic Removal*	*Source*
Coagulation/Filtration	bench		80%	Hering et al., 1997
	full	$FeCl_3$	81-96%	Scott et al., 1995
	full	Alum	23-71%	"
	full	Alum	< 50%	McNeill & Edwards, 1995
	full		52%, 79% to <5 µg/L	EPA, 2000b
Lime Softening	full		90%	McNeill & Edwards, 1995
	pilot		100%	Sorg & Logsdon, 1978
	full	pH below 10.5	45%	EPA, 2000b
Iron Removal	full		80-95%	McNeill & Edwards, 1995
	full		87%, 74%	EPA, 2000e
Ion Exchange	pilot		<2 µg/L	Clifford, 1999
	POU		<5 µg/L	Fox & Sorg, 1987, 1989
	full		53%, 97%	EPA, 2000f
Activated Alumina	POU		<5 µg/L	Fox & Sorg,1987, 1989
	pilot		<5 µg/L	Hathaway & Rubel, 1987
	full		87%, 98%	EPA, 2000f
Reverse Osmosis	POU		<5 – 20 µg/L	Fox & Sorg, 1987
	bench		94.5 – 100%	Waypa et al., 1997
	pilot	As(V)	>95%	EPA, 1999

Table 7. Arsenic Treatment Technology Advantages and Disadvantages *(Sources: Clifford, 1999; Waypa et al., 1997; McNeill and Edwards, 1997b)*

Treatment Technology	*Advantages*	*Disadvantages*
Ion Exchange	• Ease of regeneration with NaCl • Familiarity with technology due to use for softening in water treatment • Product water is lower in nitrate, sulfate, chloride, and TDS which may help in meeting secondary standards • Essentially zero level of effluent As possible • Relatively insensitive to flow variations, short contact time required • Large variety of specific resins available	• Competition concern with high TDS or high sulfate waters • Large amounts of salt are used during regeneration of the resin (recycle of brine solution could reduce the amount) • Danger of using IX beyond the point of sulfate exhaustion (chromatographic effect allows exhausted exchange resin to release nearly all previously removed As back into the treated water at high concentrations)
Activated Alumina	• As is high on the selectivity sequence for AA so don't have to worry about TDS or sulfate levels like IX • Can use media on a throw-away basis or regenerate • Low effluent As level possible • Highly selective for fluoride as well as arsenic	• Some of the sorptive capacity is lost after each regeneration according to pilot studies • Must go through a complicated two step acid-base regeneration procedure which may be a problem for smaller systems • The pH must be adjusted to the 5.5-6.0 range for greatest removal efficiency which will mean addition of acid for high pH groundwaters • Higher aluminum residuals which may affect meeting secondary Al standard • Possibility of chromatographic peaking of other anions such as F because of selectivity sequence for AA • Slow adsorption kinetics and relatively long contact time required • Significant volume/mass of spent regenerant to neutralize and dispose

Table 7. (continued)

Treatment Technology	*Advantages*	*Disadvantages*
Coagulation/ Filtration	• Existing conventional water treatment for turbidity removal can also remove As if enhanced	• Increase sludge production by increasing coagulant dosage
Fe/Mn Oxidation	• Existing conventional water treatment for Fe/Mn can also remove As if enhanced	• As removal is highly dependent upon the level of Fe in the source water
Lime Softening	• Existing conventional water treatment for hardness can also remove As if enhanced	• The presence of trace amounts of orthophosphate could limit arsenate removal • The presence of carbonate could limit arsenate removal by $Mg(OH)_2$
Membrane Processes (RO, NF)	• Secondary benefits such as nitrate, chloride, sulfate, and TDS removal • High removal efficiencies for As(III) and As(V) eliminates the need for preoxidation • No need for optimization of pH because removal is pH independent (from pH 4 to 8) • Dissolved co-occurring inorganic solutes (sulfate, phosphate) don't affect removal	• Low amount of recovery (permeate water compared with concentrate water) • Difficulty controlling corrosion associated with preacidification for RO • Long-term performance and possible deterioration in performance over time due to colloidal and NOM fouling • Pretreatment of surface water may be needed to prevent fouling

Table 8. Membrane Terminology (Adapted from Taylor and Wiesner, 1999)

Term	*Definition*
Feedwater	Influent water to the membrane
Concentrate, reject, residual stream	Membrane waste stream that contains higher TDS than the feedwater
Brine	Concentrate stream containing TDS greater than 36,000 mg/L
Permeate or product	Membrane product stream that contains lower TDS than the feedwater
Membrane element	Single membrane unit
Pressure vessel	Single tube with several membrane elements in series
Stage or bank	Parallel pressure vessels
Array or train	Multiple interconnected stages in series
Rejection	% solute concentration reduction of the product stream relative to the feedwater
Flux	Mass ($mL^{-2}t^{-1}$) or volume (Lt^{-1}) rate of transfer through a membrane surface
Scaling	Precipitation of solids in an element due to solute concentration in the feedwater
Fouling	Deposition of solid material from the feedwater in a membrane element
Recovery	% of product water that can be produced from the feedwater

Table 9. Summary of Residuals/Management Methods (Source: Adapted from U.S. EPA, 2000a)

Treatment Technology	*Form of Residual*	*Type of Residual*	*Possible Disposal Methods*
Anion Exchange	Liquid	Regeneration Streams --Spent Backwash --Spent Regenerant --Spent Rinse Stream	Sanitary Sewer Direct Discharge (NPDES) Evaporation Ponds/Lagoon
	Solid	Spent Resin	Landfill Hazardous Waste Landfill Return to Vendor
Activated Alumina	Liquid	Regeneration Streams --Spent Backwash --Spent Regenerant (Caustic) --Spent Neutralization (Acid) --Spent Rinse Liquid Filtrate (when brine streams are precipitated)	Sanitary Sewer Direct Discharge (NPDES) Evaporation Ponds/Lagoon
	Solid	Spent Alumina Sludge (when brine streams are precipitated)	Landfill Hazardous Waste Landfill Land Application
Media Adsorption (GFH, Fe-coated AA, proprietary media, etc)	Liquid	Regeneration Streams --Spent Backwash --Spent Regenerant --Spent Rinse Stream	Sanitary Sewer Direct Discharge (NPDES) Evaporation Ponds/Lagoon
	Solid	Spent Media	Landfill Hazardous Waste Landfill
Enhanced Coagulation/ Filtration	Liquid	Filter Backwash	Direct Discharge (NPDES) Sanitary Sewer Evaporation Ponds/Lagoons
	Solid	Alum or ferric sludge	Land Application Landfill
Enhanced Lime Softening	Liquid	Filter Backwash	Direct Discharge (NPDES) Sanitary Sewer Evaporation Ponds/Lagoons
	Solid	Clarifier sludge	Land Application Landfill
Iron & Manganese Removal Processes	Liquid	Filter Backwash	Direct Discharge (NPDES) Sanitary Sewer Evaporation Ponds/Lagoons
	Solid	Sludge (if separated from backwash water) Spent Media	Sanitary Sewer Land Application Landfill Landfill Hazardous Waste Landfill
Membrane Processes	Liquid	Brine (reject and backwash streams)	Direct Discharge (NPDES) Sanitary Sewer Deep Well Injection Evaporation Ponds/Lagoon

Table 10. Capital and O&M Costs for Arsenic Removal Technologies At Average Flows of 0.01, 0.1, and 1-mgd (cost equations from U.S. EPA, 2001a)

Technology	*0.01 MGD*		*0.1 MGD*		*1.0 MGD*	
	Capital cost ($)	*O&M cost ($)*	*Capital cost ($)*	*O&M cost ($)*	*Capital cost ($)*	*O&M cost ($)*
Pre-oxidation – 1.5 mg/L Chlorine	14,560 (with housing)	1,204	14,560 (with housing)	1,586	14,560 (with housing)	6,000
Enhanced Coagulation/ Filtration (existing plant)	7,291	294	8,580	948	18,053	13,996
Coagulation-assisted Microfiltration	141,931	22,232	462,973	35,772	2,098,543	64,325
Enhanced Lime Softening (existing plant)	8,378	625	12,489	3,394	33,135	30,239
Activated Alumina (no pH adjustment)	15,367	6,012 (pH 7-8) 9,986 (pH 8-8.3)	61,745	23,012 (pH 7-8) 42,358 (pH 8-8.3)	430,498	200,524 (pH 7-8) 380,164 (pH 8-8.3)
Activated Alumina (pH adjusted to 6.0)	47,661	7,448 (23,100 BV) 8,379 (15,400 BV)	97,686	22,326 (23,100 BV) 26,863 (15,400 BV)	502,904	177,081 (23,100 BV) 219,205 (15,400 BV)
Anion Exchange (< 20 mg/L SO_4)	22,992	5,766	68,612	12,073	349,648	52,187
Anion Exchange (20-50 mg/L SO_4)	24,088	9,390	110,607	17,107	437,411	71,040
Greensand Filtration	12,390	7,982	85,324	13,285	587,584	66,314

APPENDIX B

FIGURES DISCUSSED IN BODY OF REPORT

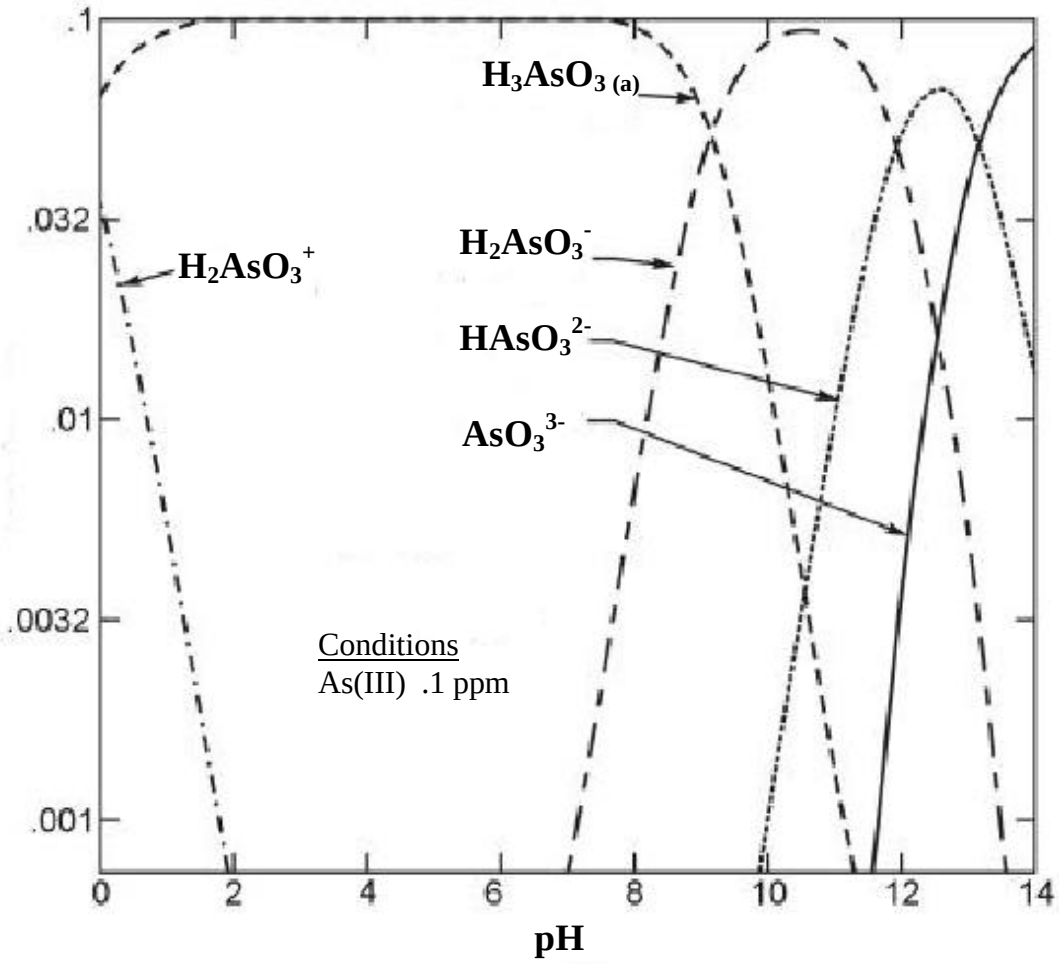

Figure 1. Arsenic (III) Solubility Diagram *(Source: U.S. Environmental Protection Agency. Arsenic Removal from Drinking Water by Coagulation/Filtration and Lime Softening Plants, NRMRL-ORD, EPA/600/R-00/063 (June 2000b).*

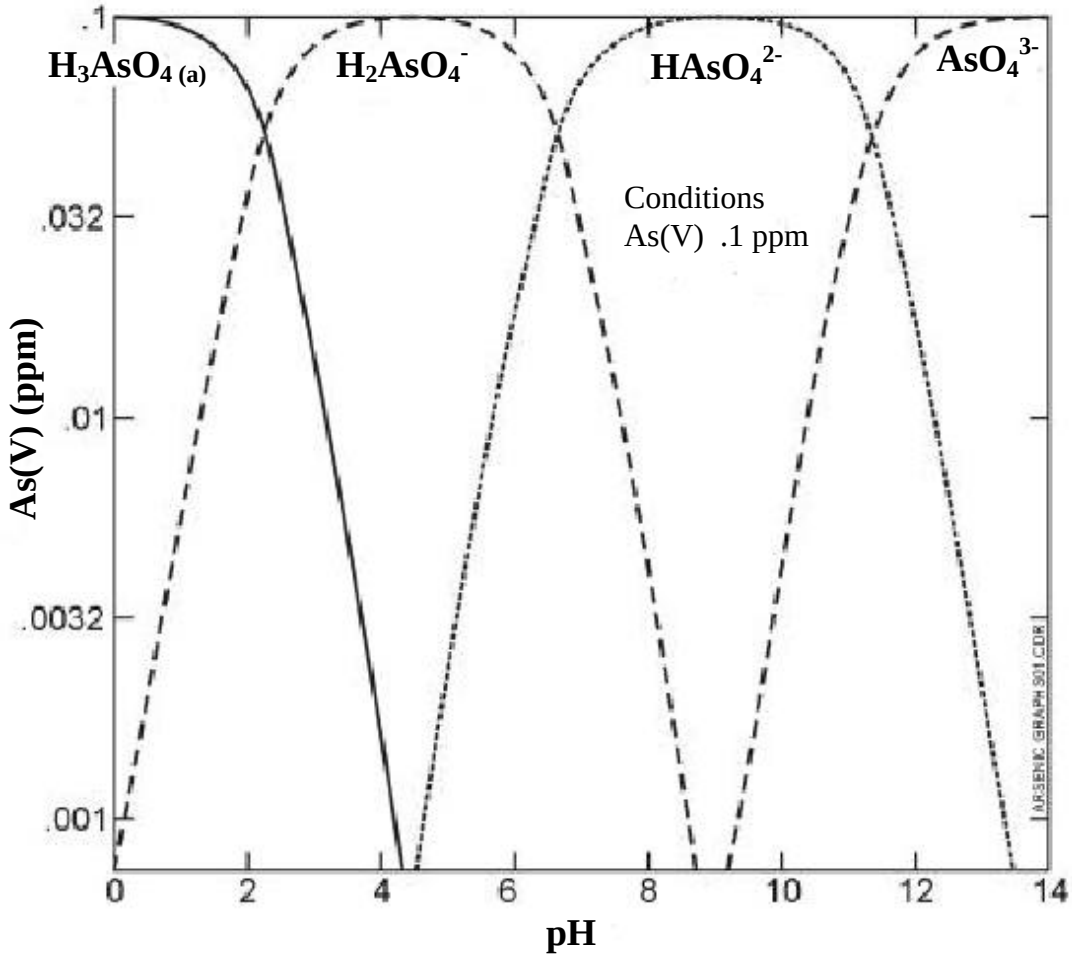

Figure 2. Arsenic (V) Solubility Diagram *(Source: U.S. Environmental Protection Agency. Arsenic Removal from Drinking Water by Coagulation/Filtration and Lime Softening Plants, NRMRL-ORD, EPA/600/R-00/063 (June 2000b).*

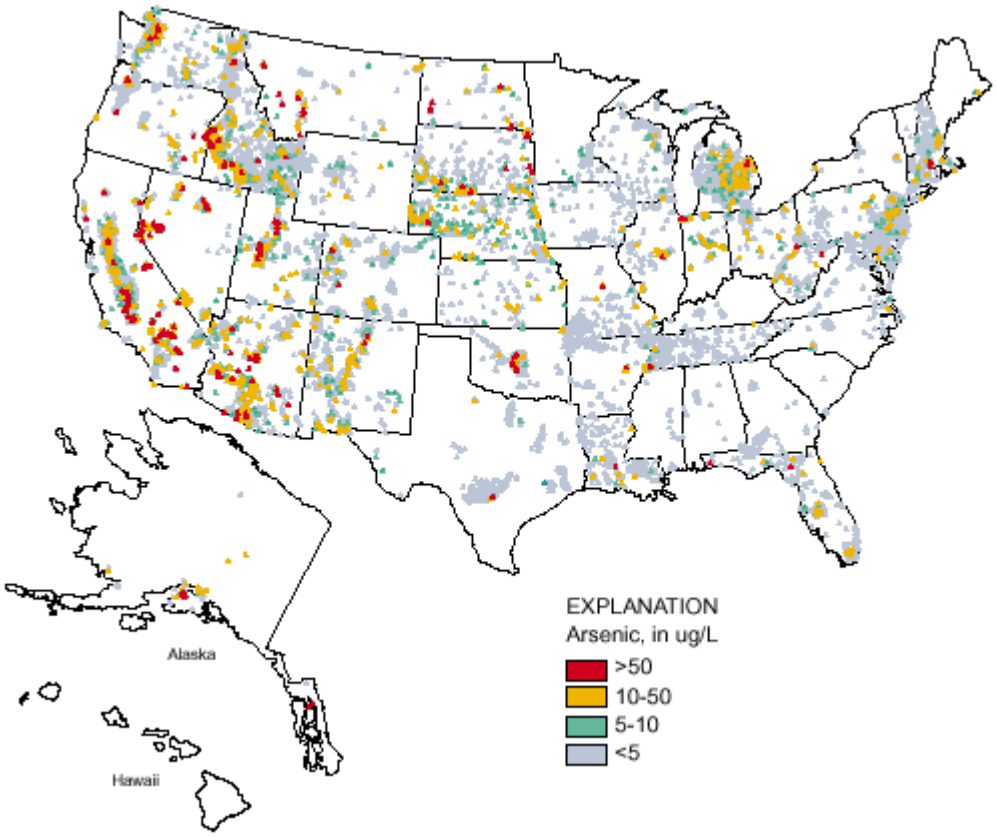

Figure 3. Arsenic Concentrations in Groundwater of the United States *(Source: U.S. Geological Survey. Arsenic in Ground-Water Resources of the United States. Fact Sheet FS-063-00, May 2000)*

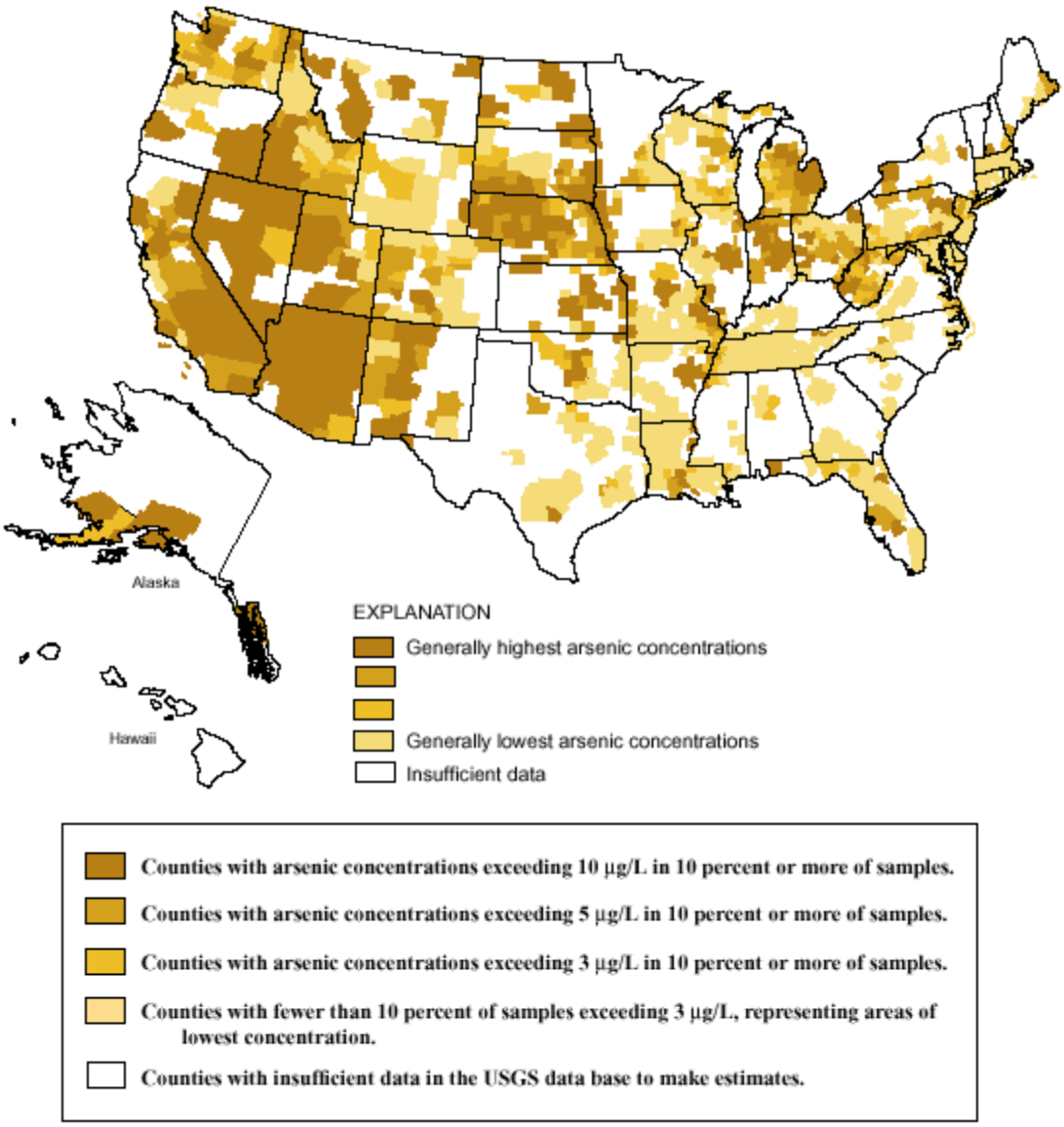

Figure 4. Counties With Arsenic Concentrations Exceeding Possible New MCLs in 10 Percent or More of Groundwater Samples *(Source: U.S. Geological Survey. Arsenic in Ground-Water Resources of the United States. Fact Sheet FS-063-00, May 2000)*

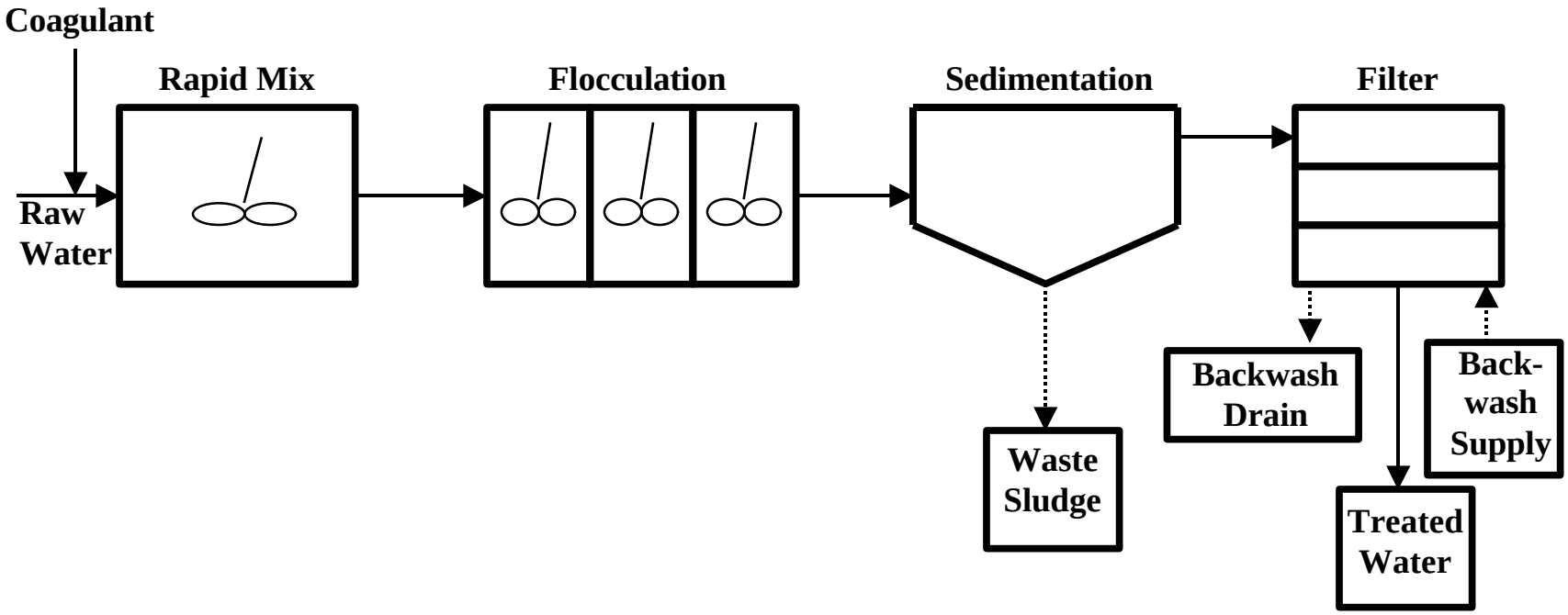

Figure 5. Typical Coagulation/Filtration Treatment Process Diagram

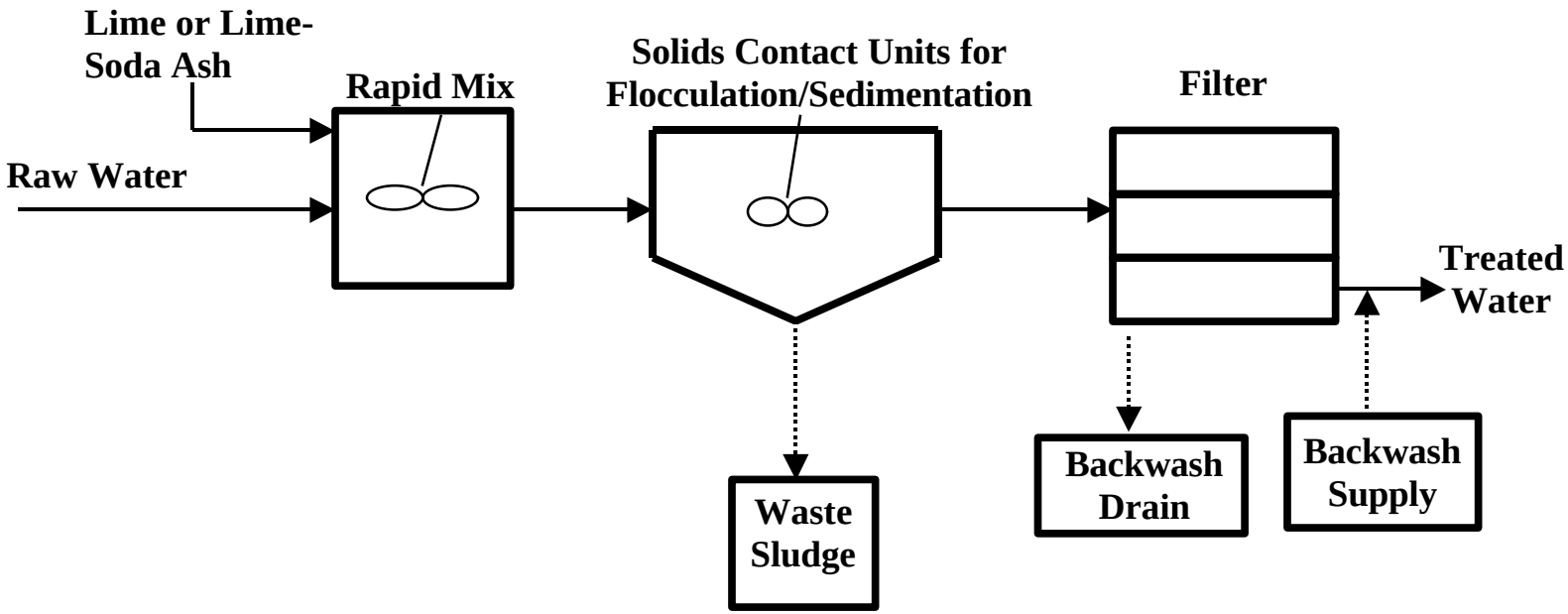

Figure 6. Typical Lime Softening Treatment Process Diagram

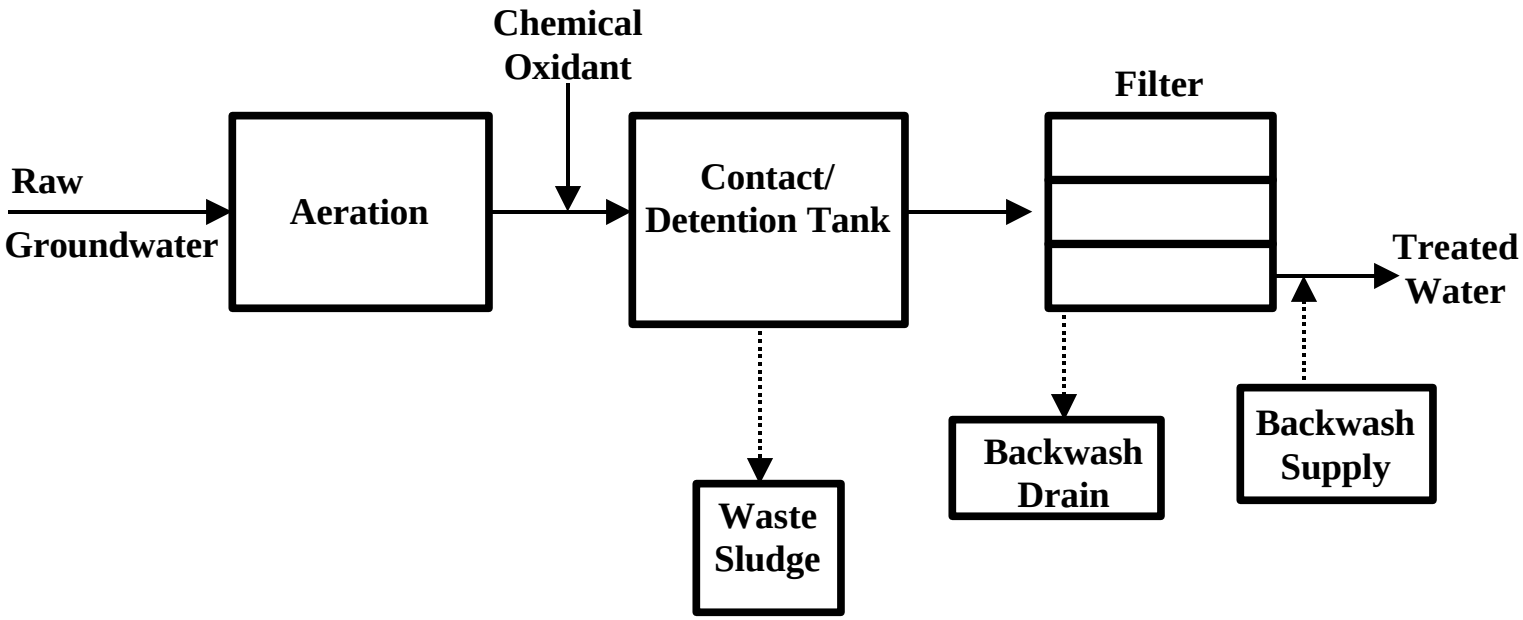

Figure 7. Typical Fe/Mn Removal Treatment Process Diagram

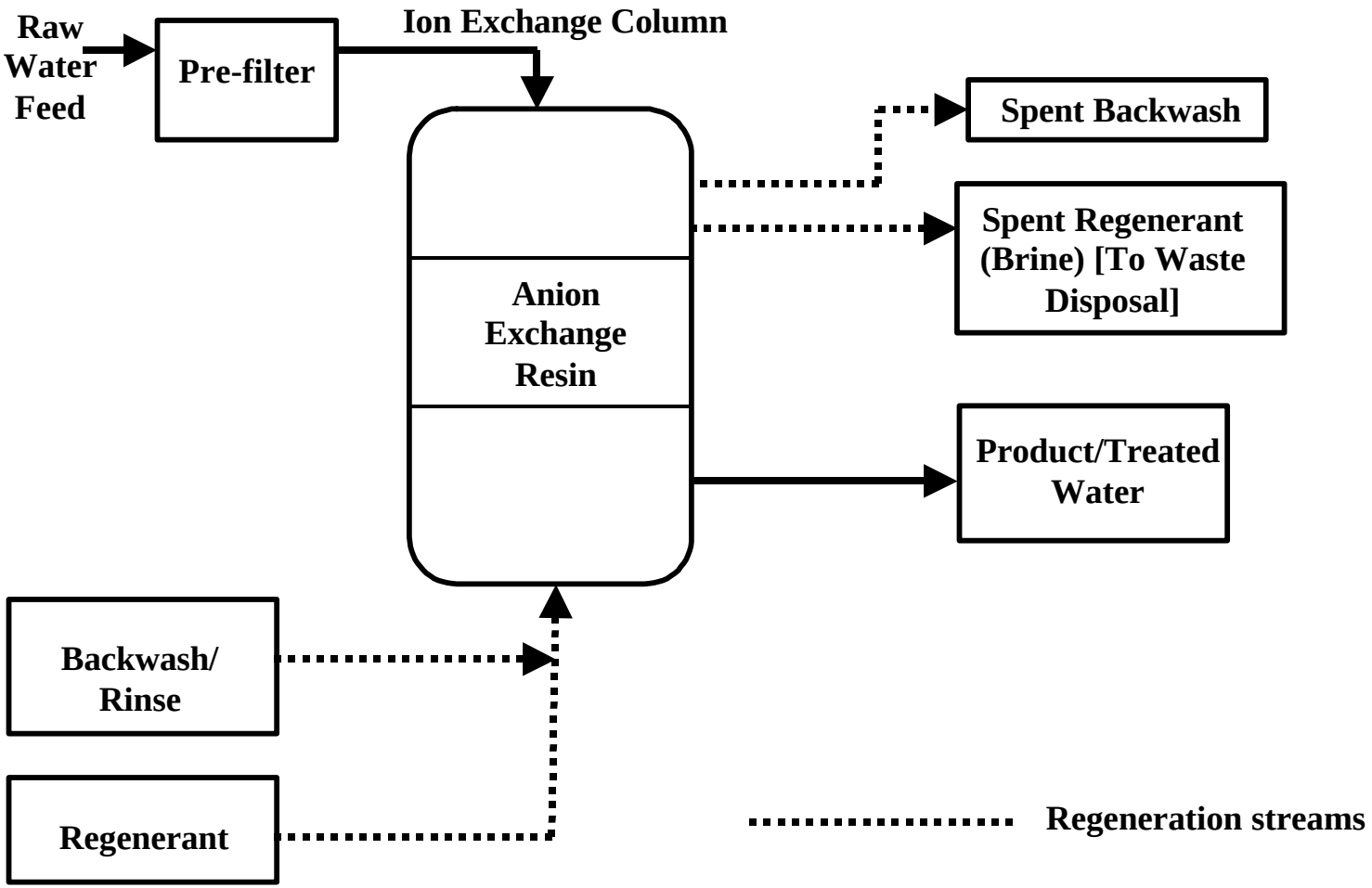

Figure 8. Typical Anion Exchange Treatment Process Diagram (Adapted from U.S. EPA, 2000a)

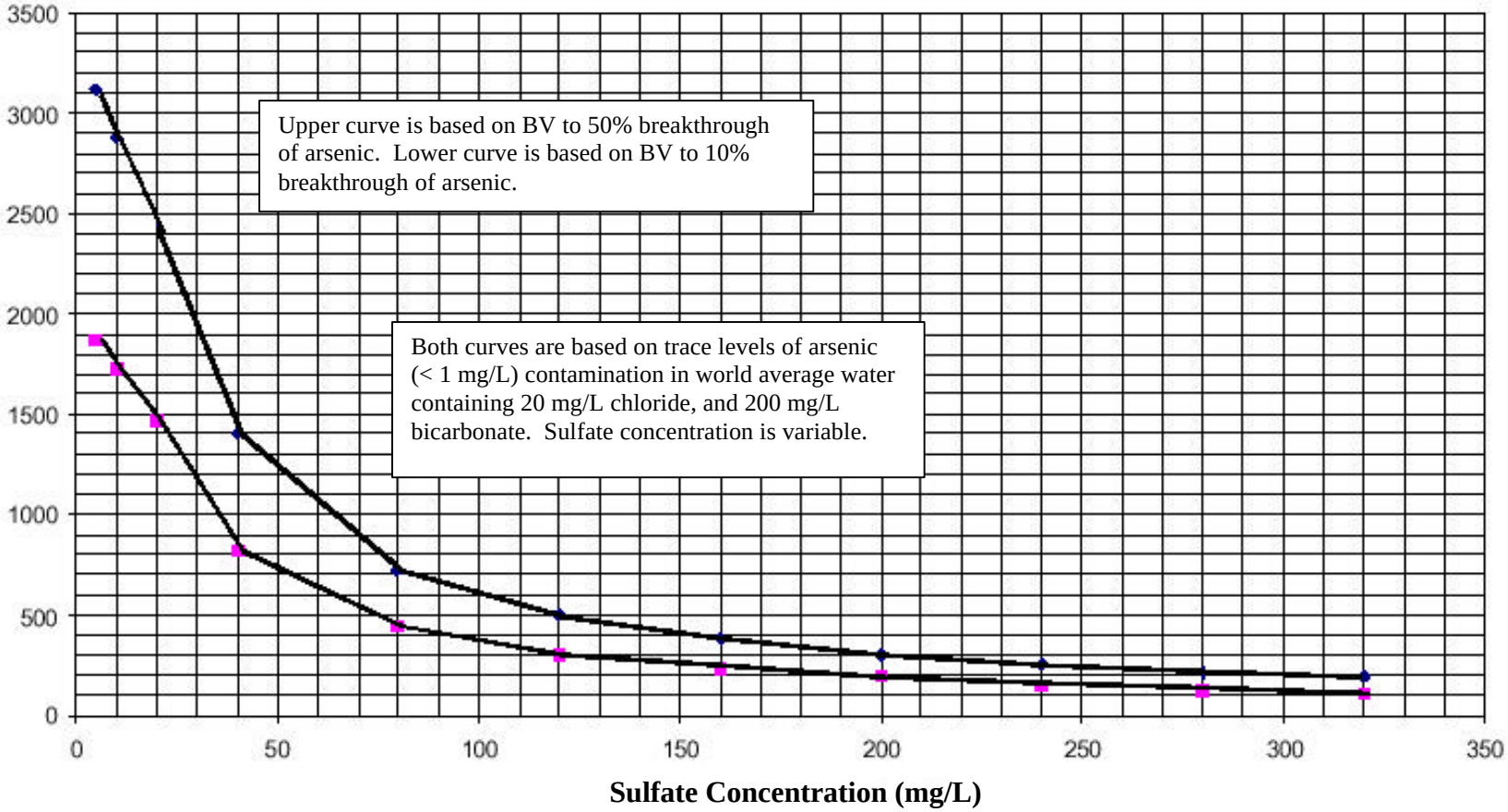

Figure 9. Bed Volumes to Arsenic Breakthrough as a Function of Sulfate Concentration for Ion Exchange (Source: U.S. EPA, 2001a)

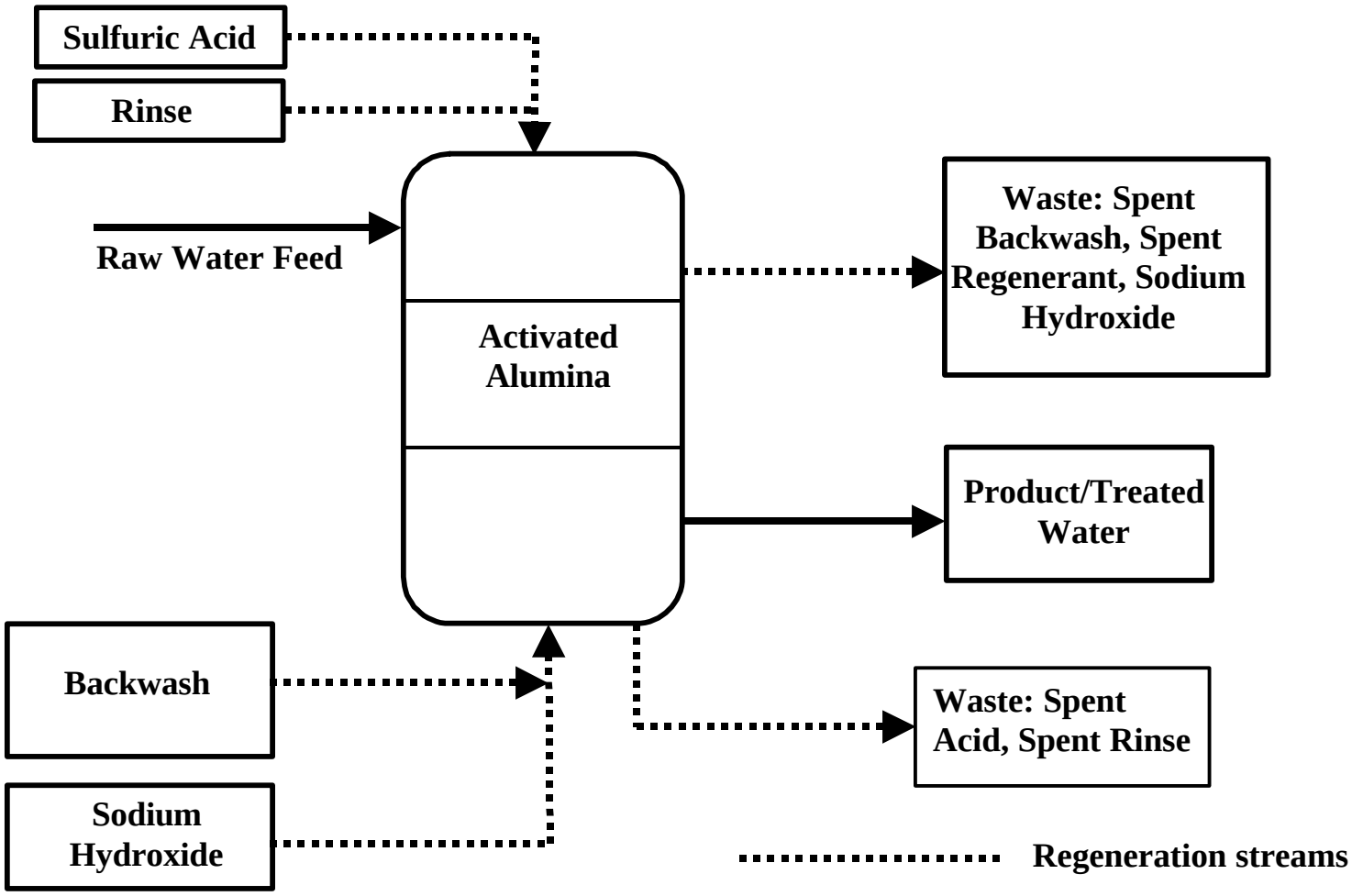

Figure 10. Typical Activated Alumina Treatment Process Diagram (Adapted from U.S. EPA,2000a)

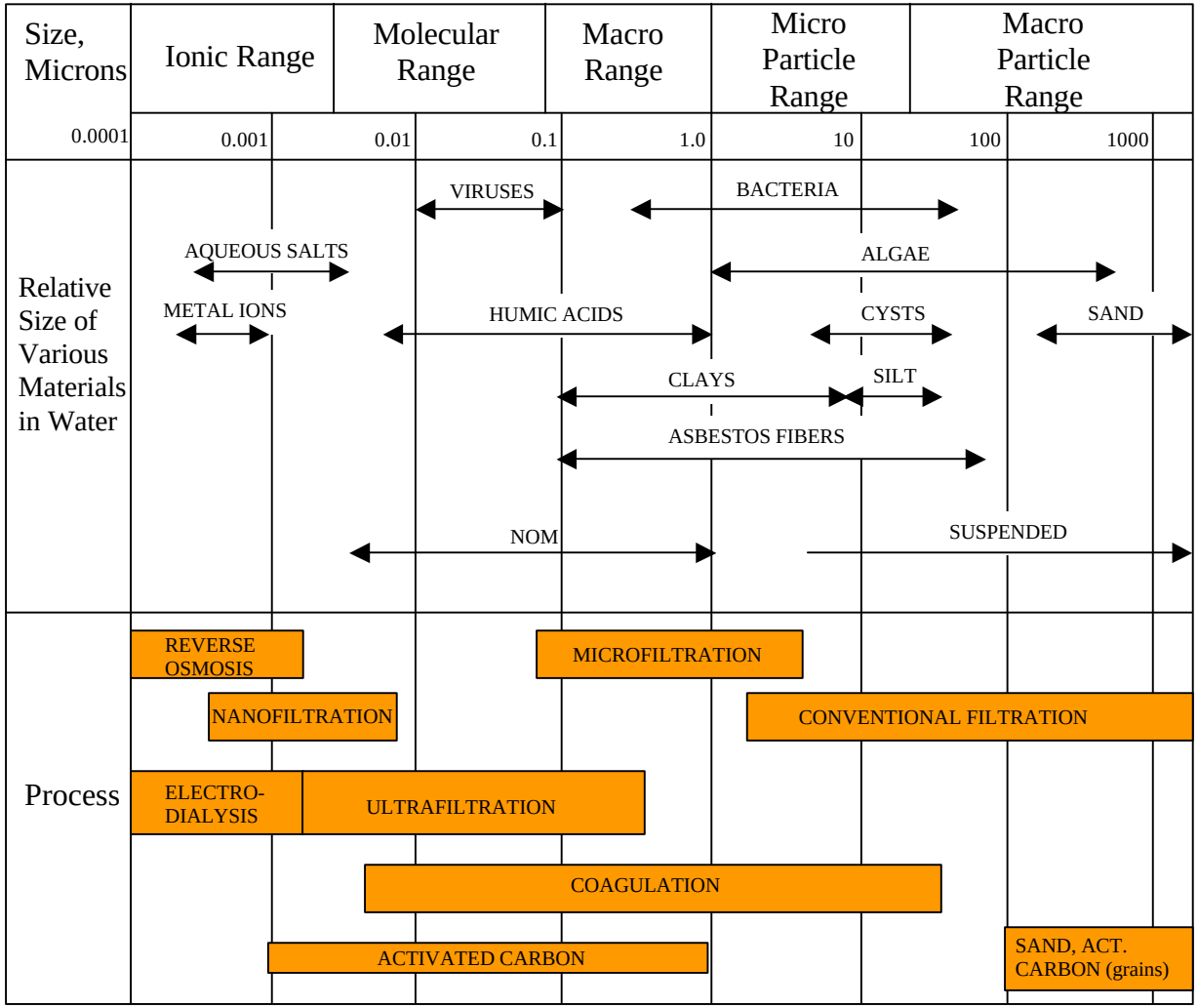

Figure 11. Size Ranges of Membrane Processes and Contaminants (Adapted from Taylor and Wiesner, 1999)

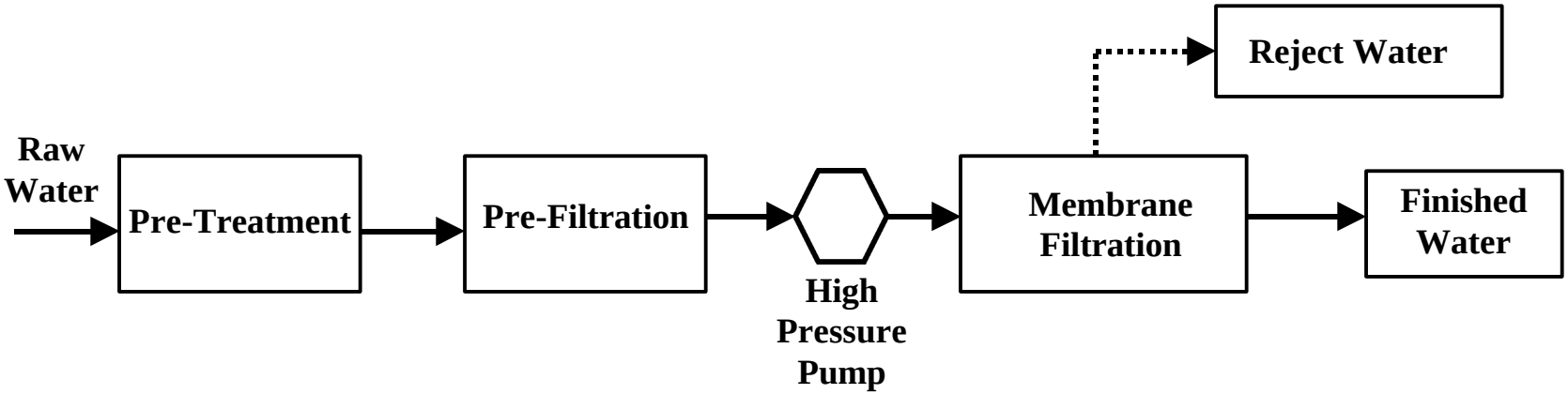

Figure 12. Typical NF/RO/EDR Membrane Filtration Treatment Process Diagram (Adapted from U.S. EPA, 2000a)

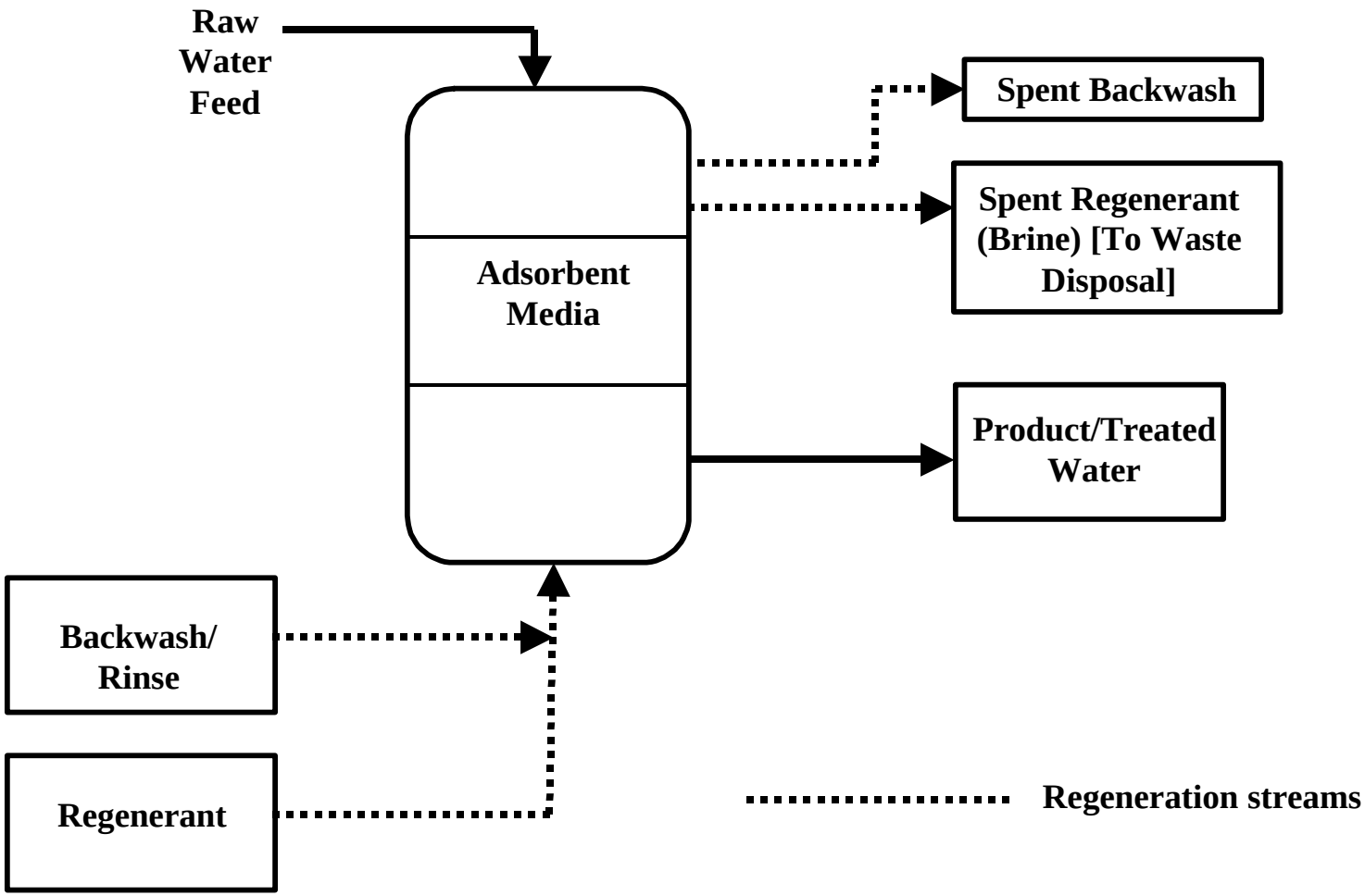

Figure 13. Typical Media Adsorption Treatment Process Diagram (Adapted from U.S. EPA, 2000a)

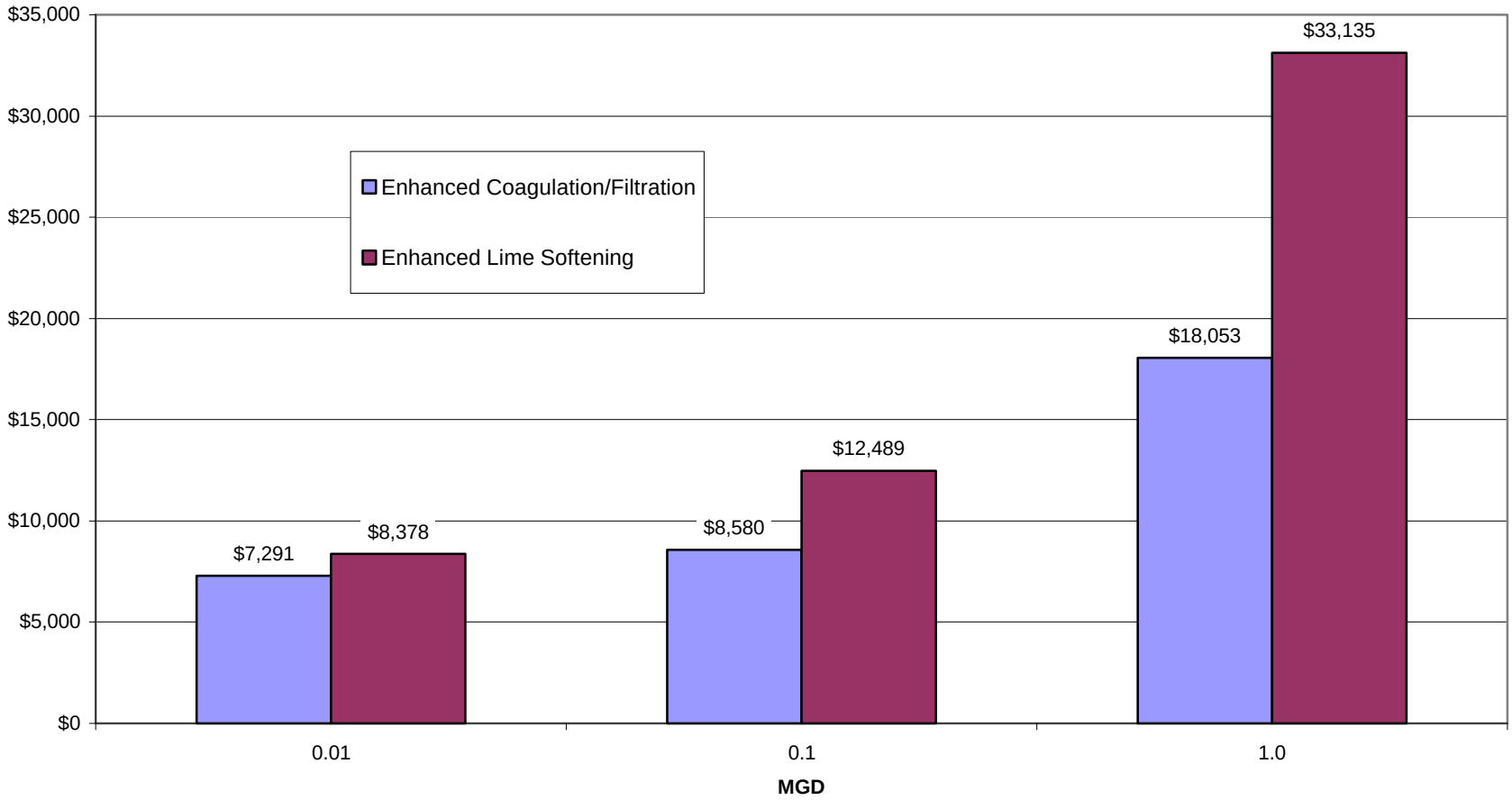

Figure 14. Enhanced Coagulation/Filtration and Enhanced Lime Softening Capital Costs

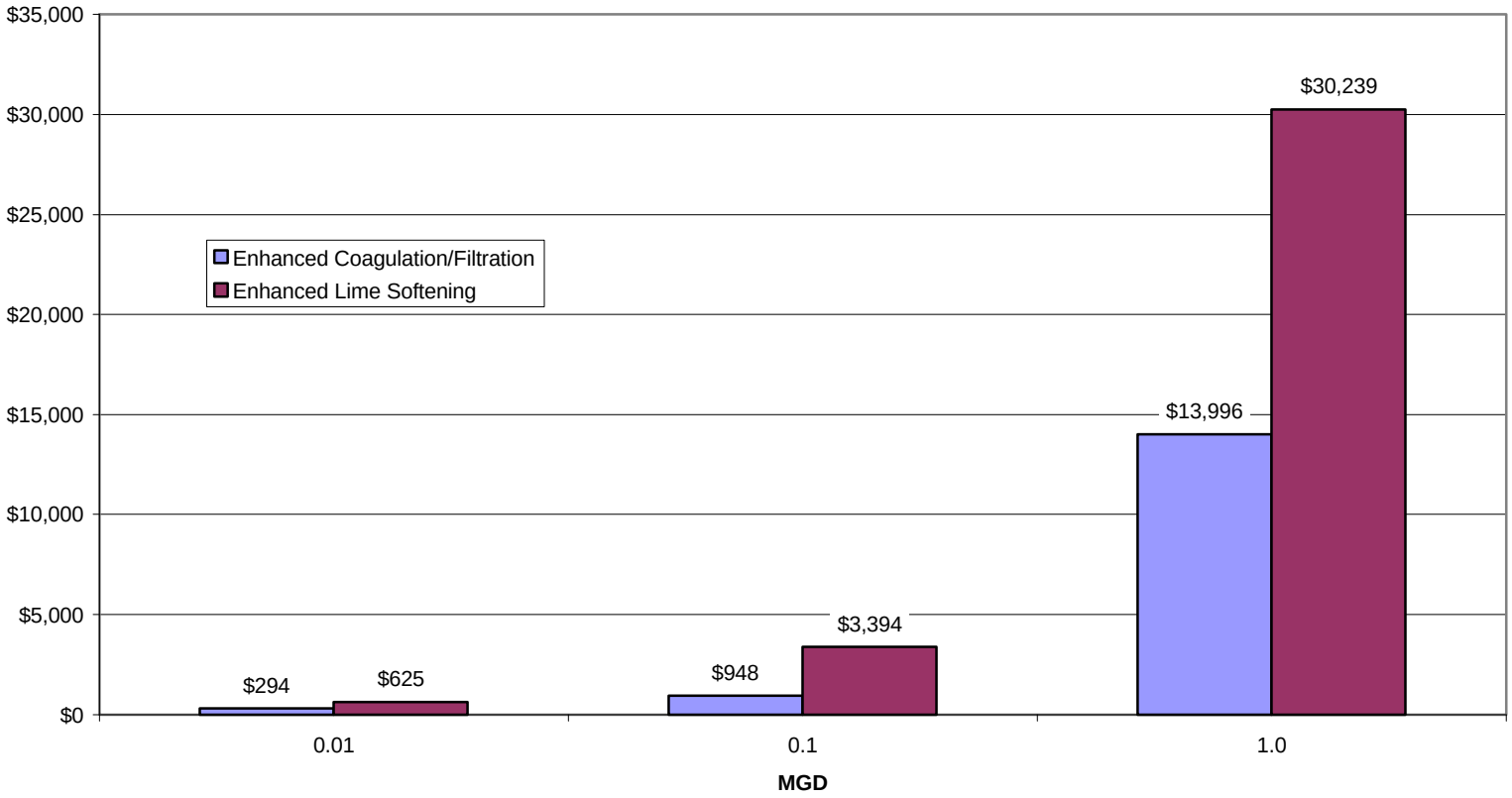

Figure 15. Enhanced Coagulation/Filtration and Enhanced Lime Softening O&M Costs

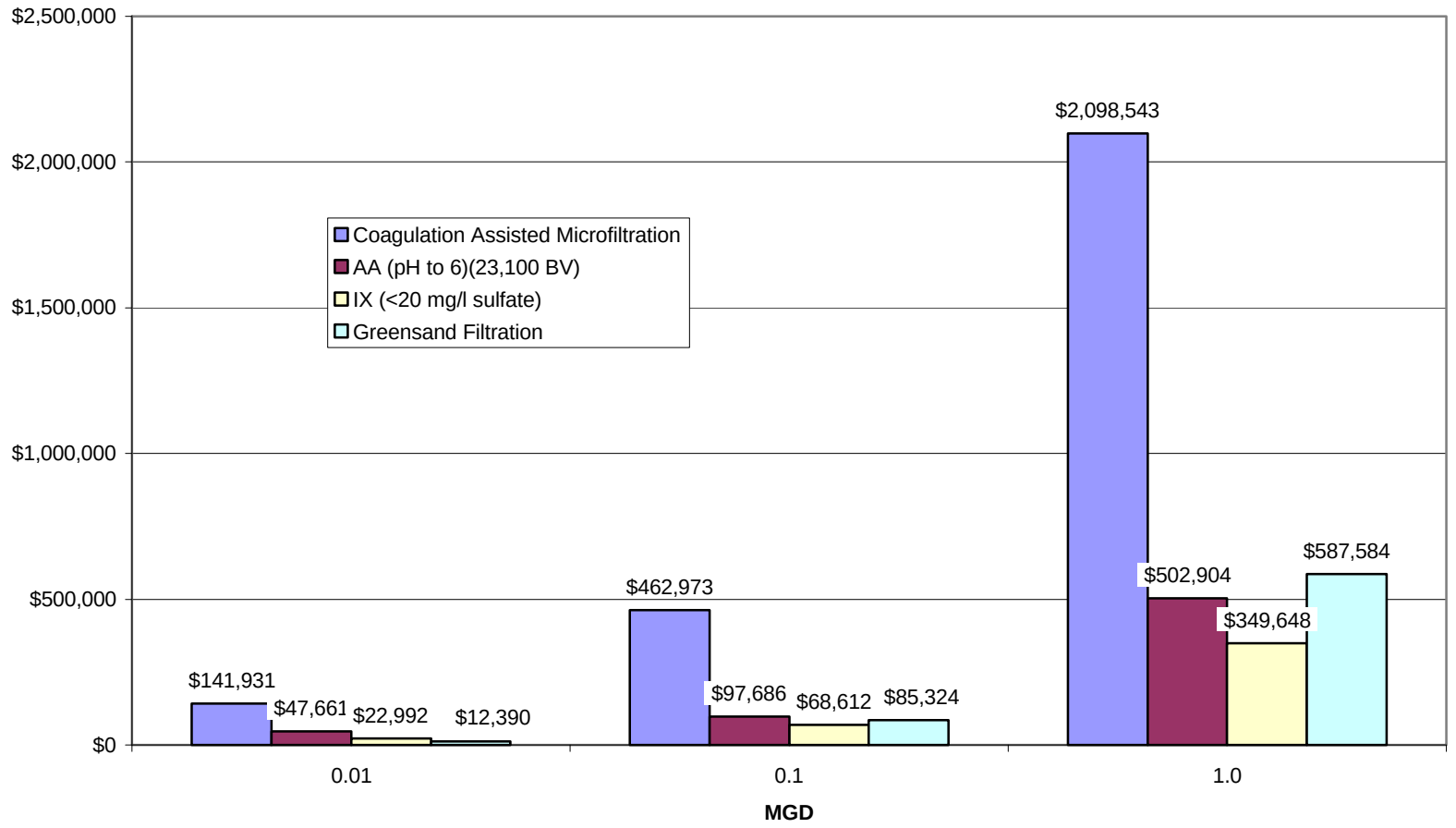

Figure 16. C/MF, AA, IX, and Greensand Filtration Capital Costs

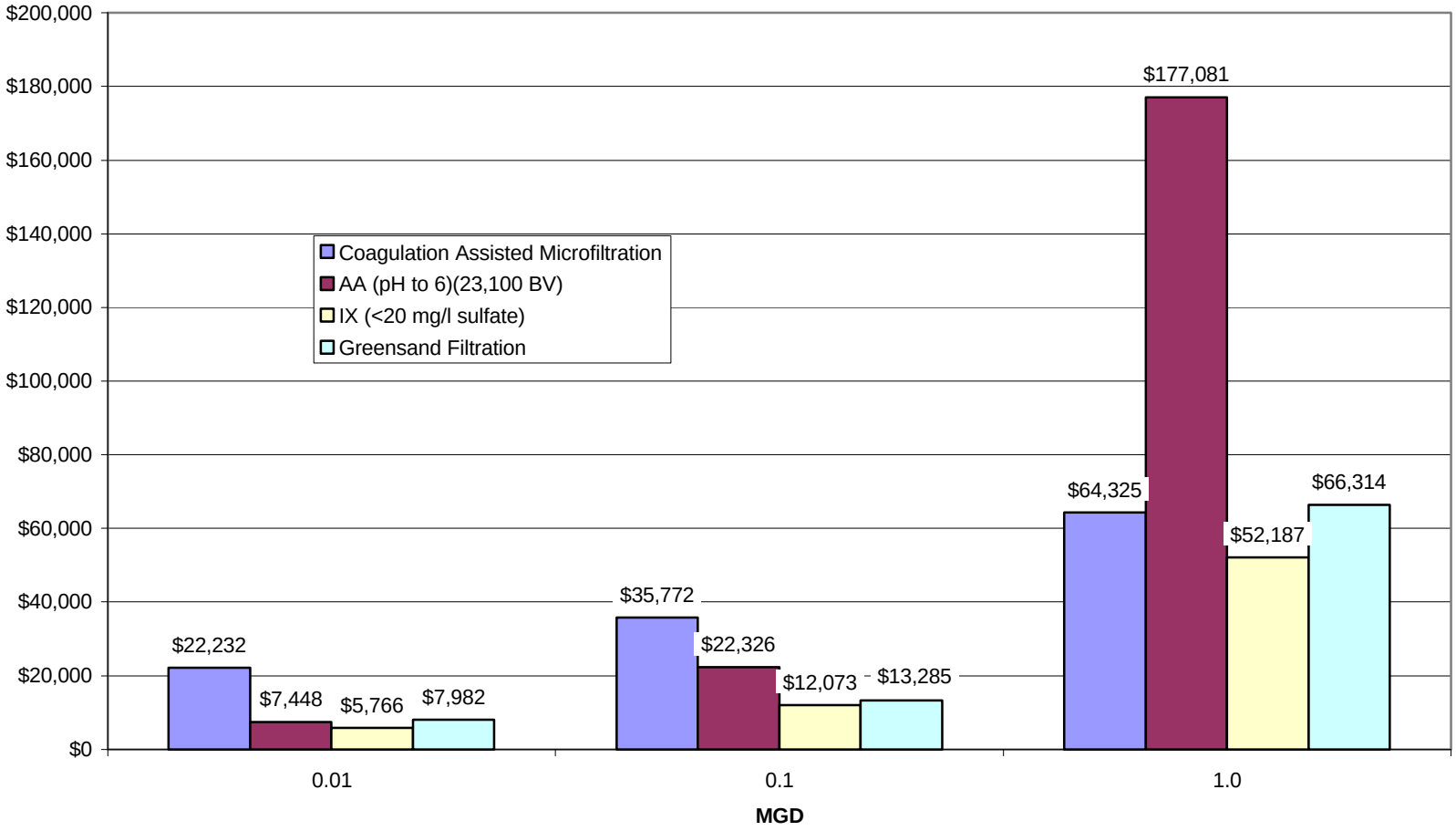

Figure 17. C/MF, AA, IX, and Greensand Filtration O&M Costs

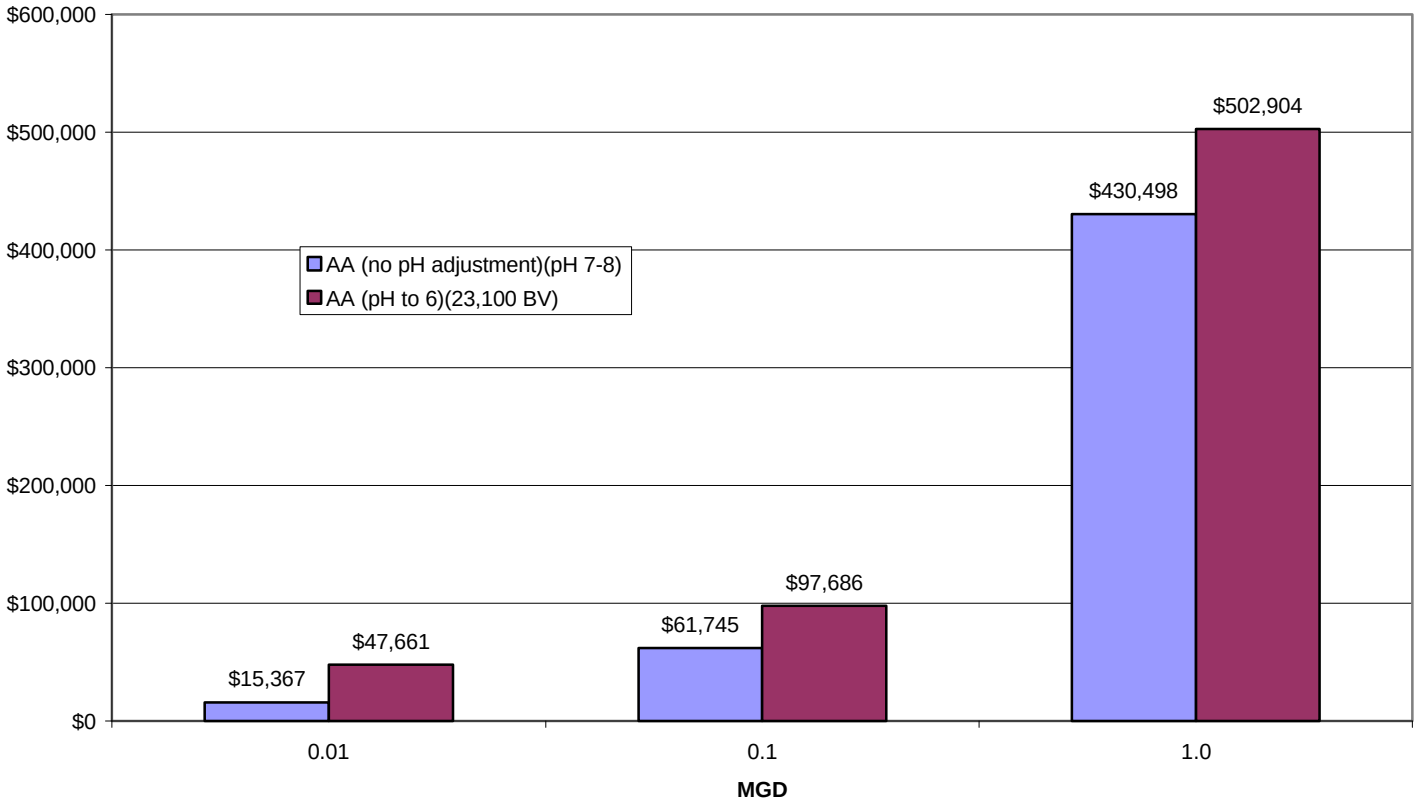

Figure 18. AA With and Without pH Adjustment Capital Costs

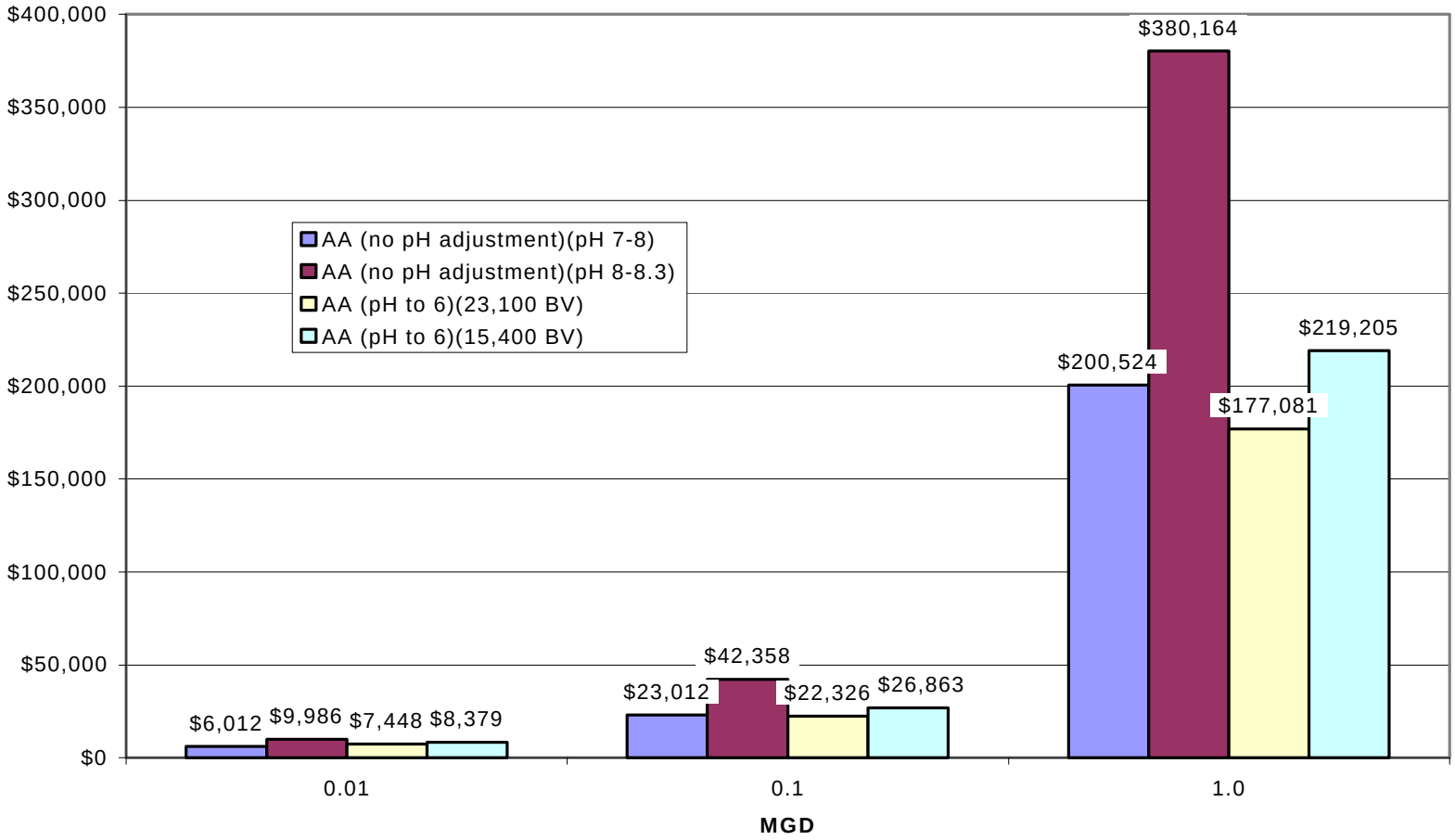

Figure 19. AA With and Without pH Adjustment O&M Costs

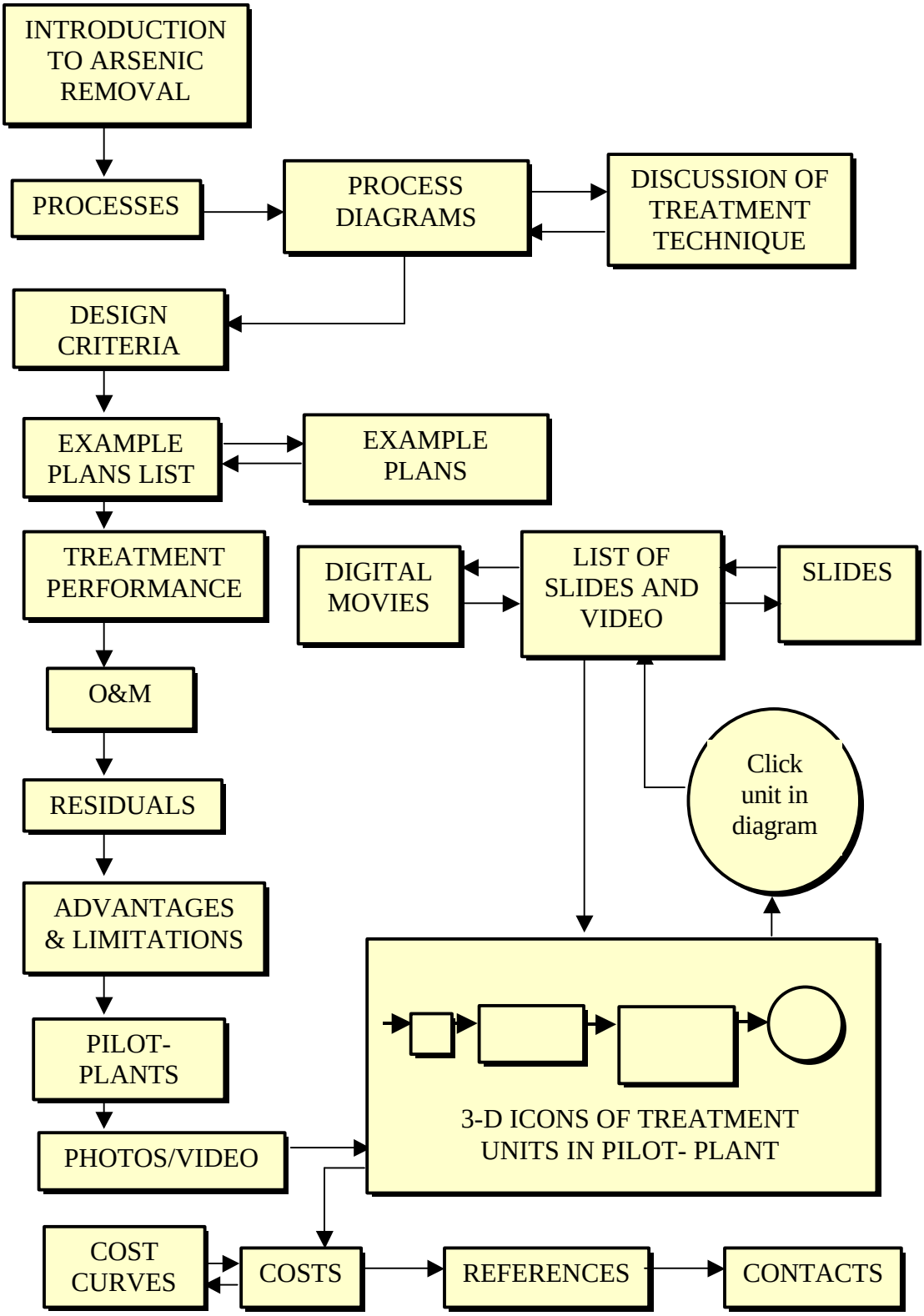

Figure 20. Flow Chart of Arsenic Removal Module

APPENDIX C

CORRESPONDENCE WITH PILOT-PLANT OWNERS

December 18, 2000

Mr. Ramesh Narasimhan, P.E.
Narasimhan Consulting Services
3150 N. 24th Street, Suite D-104
Phoenix, Arizona 85016

Re: Visit to Phoenix pilot-plant facility

Dear Mr. Narasimhan:

I believe that Greg Harrison, who is working for me on a project, talked with you about visiting one of NCS's projects, the City of Phoenix pilot-plant arsenic removal facility. Our purpose in visiting the facility is to take photos and video of the plant. The photos and video will be incorporated into an educational CD-ROM on small water supply technology. This work is funded through a grant provided by the University of New Hampshire's Small Public Water Supply Technology Assistance Center which is a new center funded by the U.S. Environmental Protection Agency and managed by Robin Collins. We will develop CD-ROM's on two other small water system technologies as well including slow sand filtration and iron and manganese control. We have already visited slow sand filtration plants in Vermont and New Hampshire, and visited Fe/Mn removal and sequestration plants in Ohio. These CD-ROM's will be distributed to federal and state regulatory agencies and several national and regional water system associations and societies. It is planned that these educational CD-ROMs will also be made available to small water systems, engineers and others at a reasonable cost through a professional society or other means. We will certainly give you a complimentary copy of the arsenic removal CD-ROM. We are very excited about developing a CD-ROM on arsenic removal and are very grateful to you for allowing us to use your facility in the CD.

I believe that Greg Harrison will make arrangements to visit your facilities within the next few weeks. His preliminary schedule is to visit the facility in late January 2001, probably either Monday, January 29th or Tuesday, January 30th, if those dates are suitable to the facilities involved. He hopes to take pictures of all the treatment processes, adsorbents, controls, chemical feed facilities, wells, etc., that may be a part of the pilot-plant facility. I hope that we can photograph and video the plants in operation and possibly the media being regenerated during our visit. Most people are shy about wanting to record any comments on videotape, but if you or any of the personnel wanted to make any comments on videotape about the challenges and future of small water systems while Greg is there, we would welcome them.

I have also included a copy of the permission to use form for the photos which we have used previously on other site visits to treatment facilities. This may be helpful to provide to the owner of the project to explain what the purpose of the photos and video will be.

Thanks again for your help.

Sincerely,

R. Bruce Robinson, Ph.D., P.E.
Professor of Civil and Environmental Engineering
Office: 865.974.7730 FAX: 865.974.2669 rbr@utk.edu

Copy: Greg Harrison

APPENDIX D

PERMISSION TO USE PHOTOS & VIDEO FORM

RELEASE FORM FOR USING PHOTOS
IN EDUCATIONAL WATER TECHNOLOGY CD-ROM's

DATE:_____

NAME: _____

TITLE: _____

ADDRESS: _____

_____

_____

We want to thank you for your hospitality in letting us take pictures and video at your water plant. As you may know, we are the process of creating educational CD-ROM's on small water supply technology through a grant provided by the University of New Hampshire's Small Public Water Supply Technology Assistance Center which is a new center funded by the U.S. Environmental Protection Agency. The first three CD's will be on iron and manganese control, slow sand filtration, and arsenic removal. These CD-ROMs will be distributed to federal and state regulatory agencies and several national and regional water system associations and societies. It is planned that these educational CD-ROMs will also be made available to small water systems, engineers and others at a reasonable cost.

As part of these CD-ROM's, I would like permission to use the photos that we took that have you in them. The photos would of course be used in a professional manner. We can provide you copies of these photos if you so desire. To the extent that we can and is necessary, we will touch up the photos to remove glares, etc. and otherwise enhance their quality before incorporating them into the CD-ROM's.

I am requesting world rights to use these photos in the CD-ROM(s) and any future versions of the CD-ROM(s). Unless you request otherwise, we would identify you in the photos using your name and title as provided by you above.

If you are willing to grant us the requested permission, please sign the agreement block signed below, or send me your own signed agreement form. We may wish to convert all or some of the educational CD-ROM's to a web format so that anyone can view them online on the World Wide Web. I would like to ask your permission at this time to use the photos in this format as well and I have separated the two permission requests below.

I would like to thank you in advance for your willingness to provide permission to use the photos in our CD-ROM's and/or web site which should be a valuable resource for regulators, engineers, and water utilities. If you have any questions, please do not hesitate to call me.

Sincerely,

R. Bruce Robinson, Ph.D., P.E.
Professor of Civil and Environmental Engineering
Office: 865/974-7730 FAX: 865/974-2669
E-mail: rbr@utk.edu

CD-ROM Agreement

I hereby grant the above requested permission for use in the educational CD-ROM(s) as discussed herein.

Date: _____ Signature: _____

Web Site Agreement

I hereby grant the above requested permission for use in the educational web site as discussed herein.

Date: _____ Signature: _____

APPENDIX E

STORYBOARD

SMALL PUBLIC WATER SYSTEM TECHNOLOGY GUIDES: Vol. I

Title screen and credits

Common frame for all pages in all CD's.
Frame choices: Pipes & joints?

Please click on one of the choices below with the right mouse button

About the Small Public Water Supply Assistance Center Technology Guides Series

Slow Sand Filtration
Iron and Manganese Control
Arsenic Removal

SPWS TAC

Help
About
Quit

Developed by the Small Public Water Supply Technology Assistance Center,
The University of New Hampshire, Durham, NH
Funded through a grant from the United States Environmental Protection Agency, Grant No. ############

LOGO OF THE

Main menu page

ARSENIC REMOVAL: APPLICATION AND PRACTICE FOR SMALL WATER SYSTEMS

UTK LOG

Overview and statement of objectives

Narrative:

Include mostly text from Introduction in thesis here.

DIRECTI

NEXT

EXIT

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Process description main page

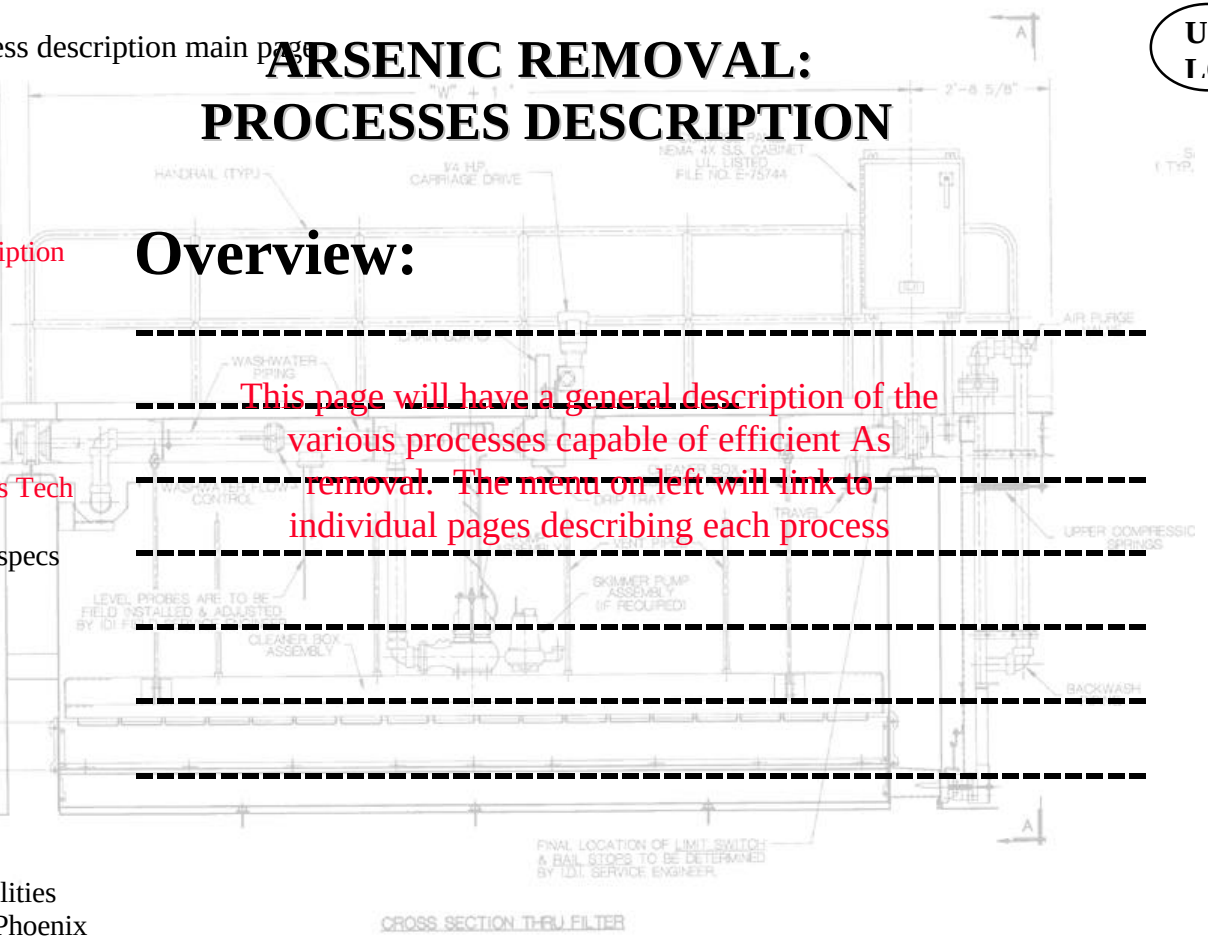
UTK LOG

ARSENIC REMOVAL: PROCESSES DESCRIPTION

- Introduction
- Processes description
  - IX
  - AA
  - Enhanced C/F
  - Enhanced LS
  - Fe Removal
  - Membranes
  - Innovative Ads Tech
- Design criteria
- Example plans/specs
- Performance
- Operation
- Automation
- Advantages, Limitations & Concerns
- Pilot-plants
- Costs
- References
- Contacts & facilities
- Virtual tour of Phoenix & Tucson pilot-plants

Overview:

This page will have a general description of the various processes capable of efficient As removal. The menu on left will link to individual pages describing each process



BACK NEXT EXIT

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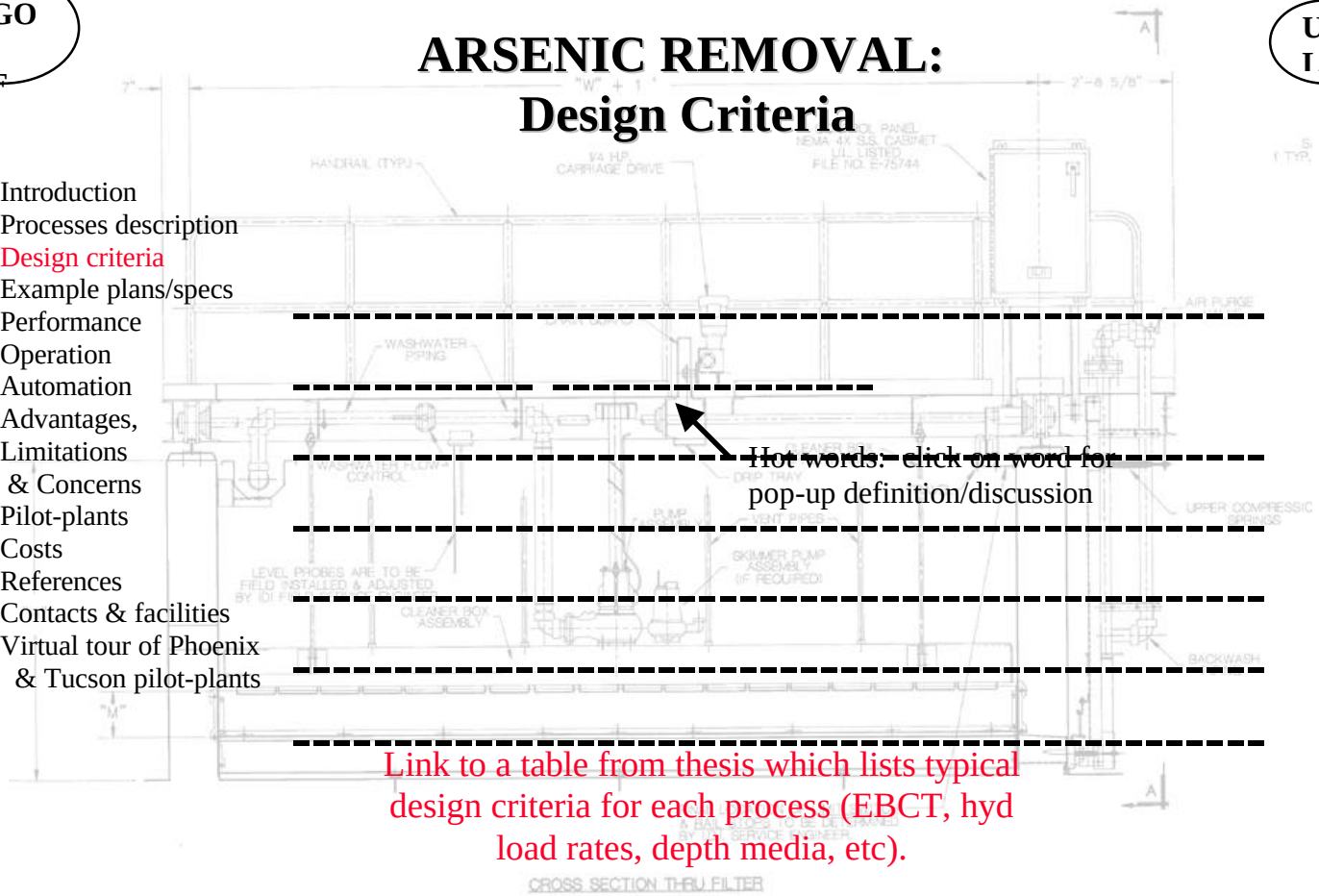
UTK LOG

ARSENIC REMOVAL:
Design Criteria



- Introduction
- Processes description
- Design criteria
- Example plans/specs
- Performance
- Operation
- Automation
- Advantages, Limitations & Concerns
- Pilot-plants
- Costs
- References
- Contacts & facilities
- Virtual tour of Phoenix & Tucson pilot-plants

Hot words: click on word for pop-up definition/discussion

Link to a table from thesis which lists typical design criteria for each process (EBCT, hyd load rates, depth media, etc).

BACK NEXT EXIT

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UTK LOG

ARSENIC REMOVAL:
Example Plans and Specifications

- Introduction
- Processes description
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- Example plans/specs
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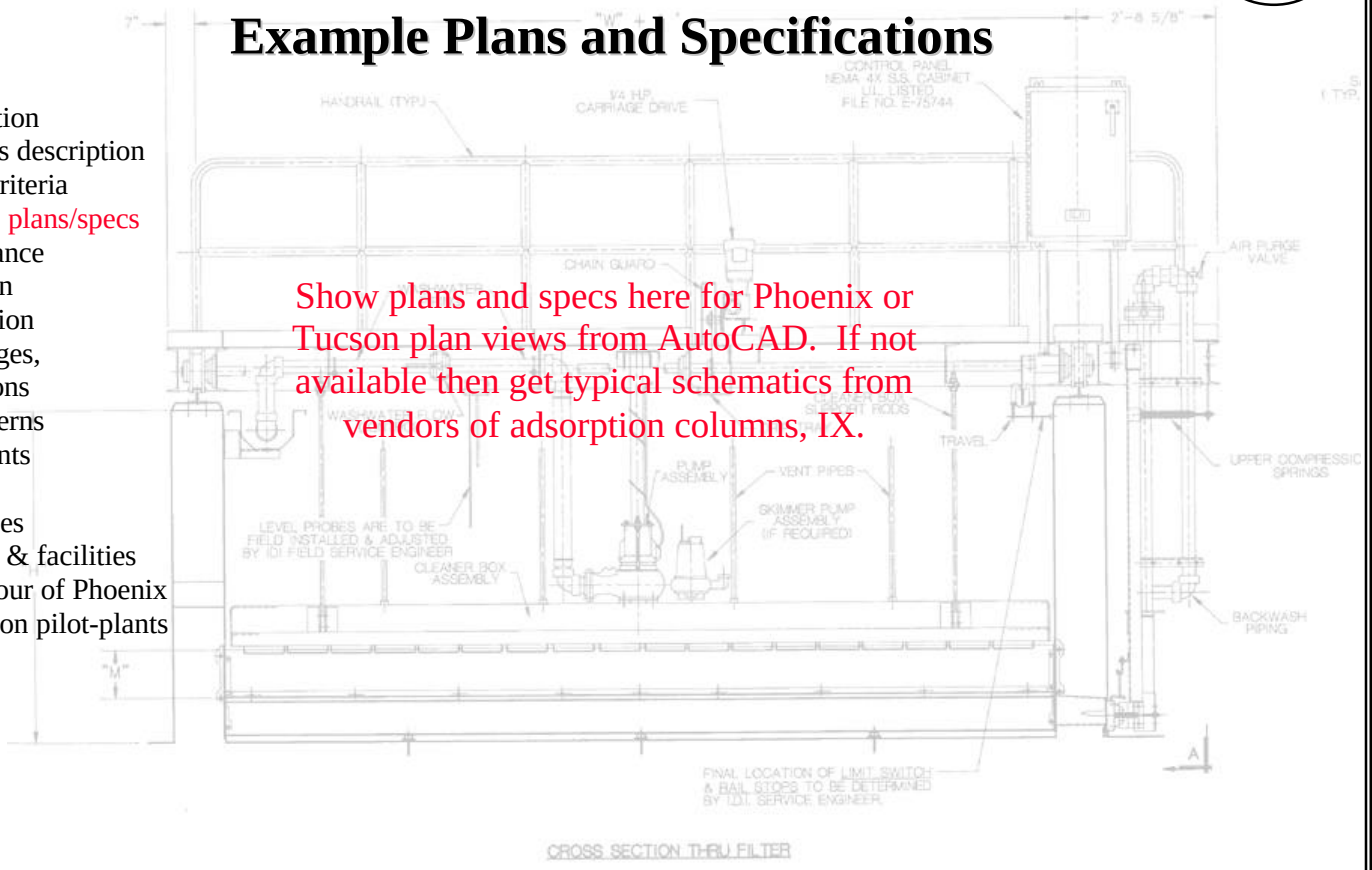
- Pilot-plants
- Costs
- References
- Contacts & facilities
- Virtual tour of Phoenix & Tucson pilot-plants

Show plans and specs here for Phoenix or Tucson plan views from AutoCAD. If not available then get typical schematics from vendors of adsorption columns, IX.



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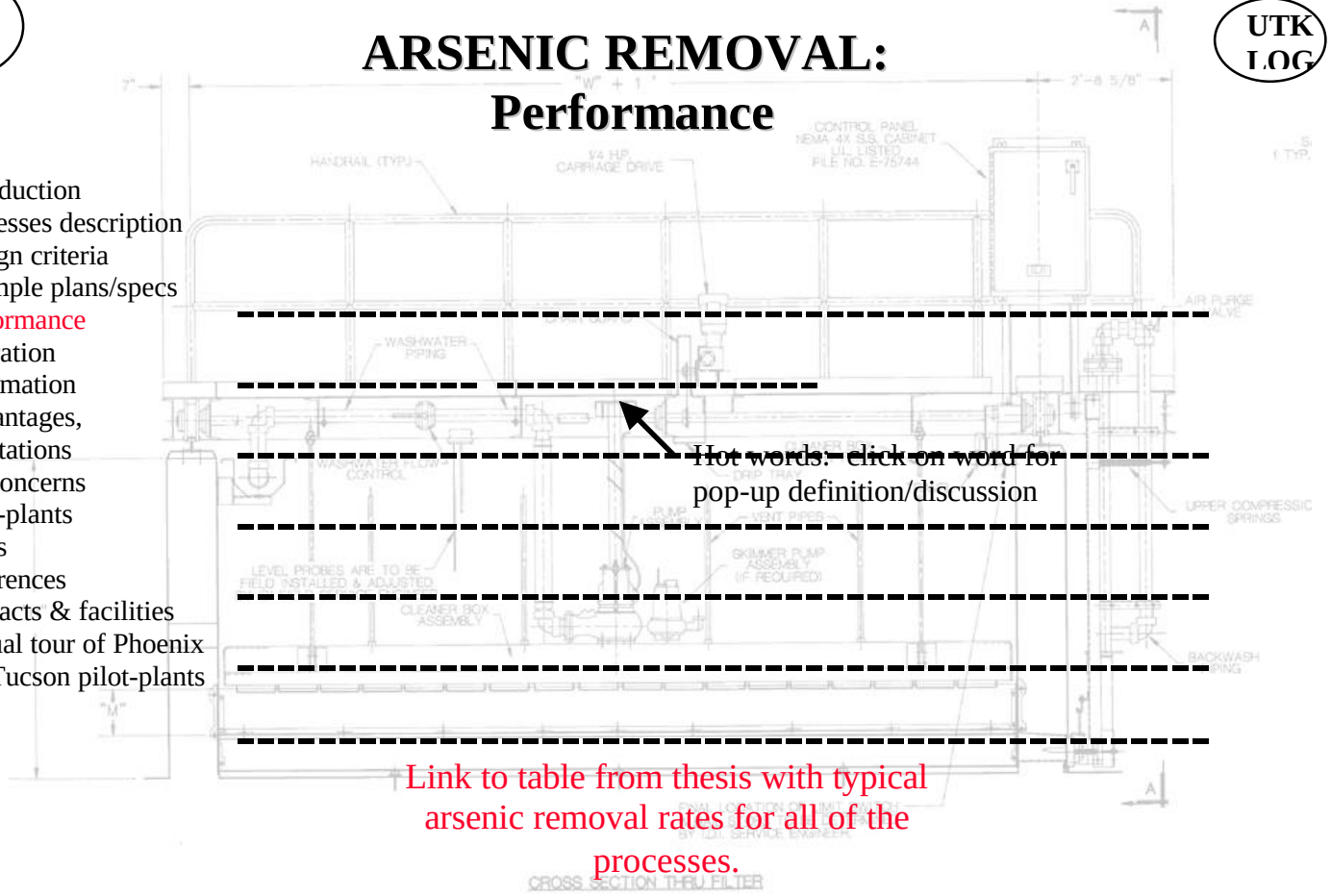
UTK LOG

ARSENIC REMOVAL:
Performance



- Introduction
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Hot words: click on word for pop-up definition/discussion

Link to table from thesis with typical arsenic removal rates for all of the processes.

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ARSENIC REMOVAL:
Operation

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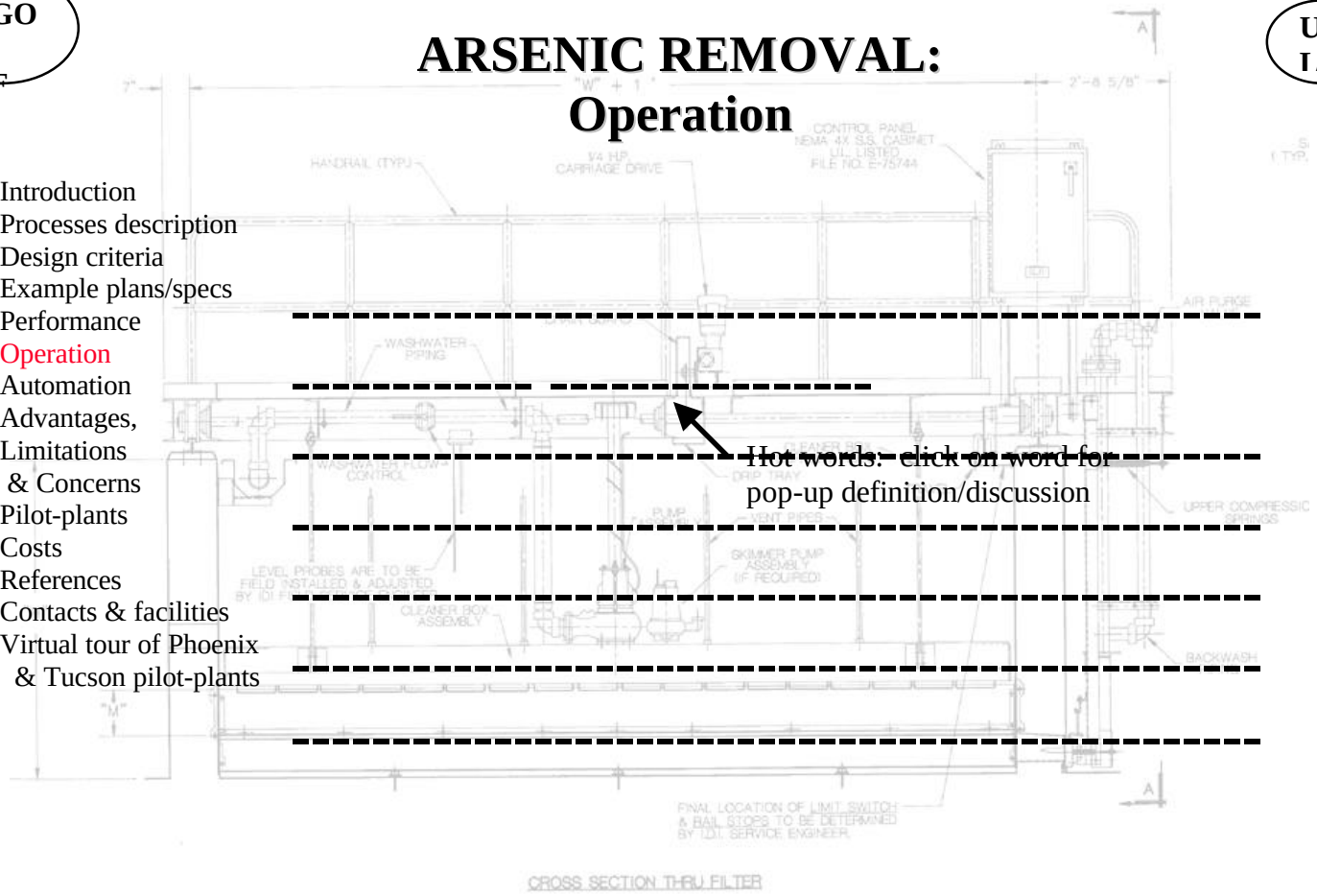
Hot words: click on word for pop-up definition/discussion



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Automation

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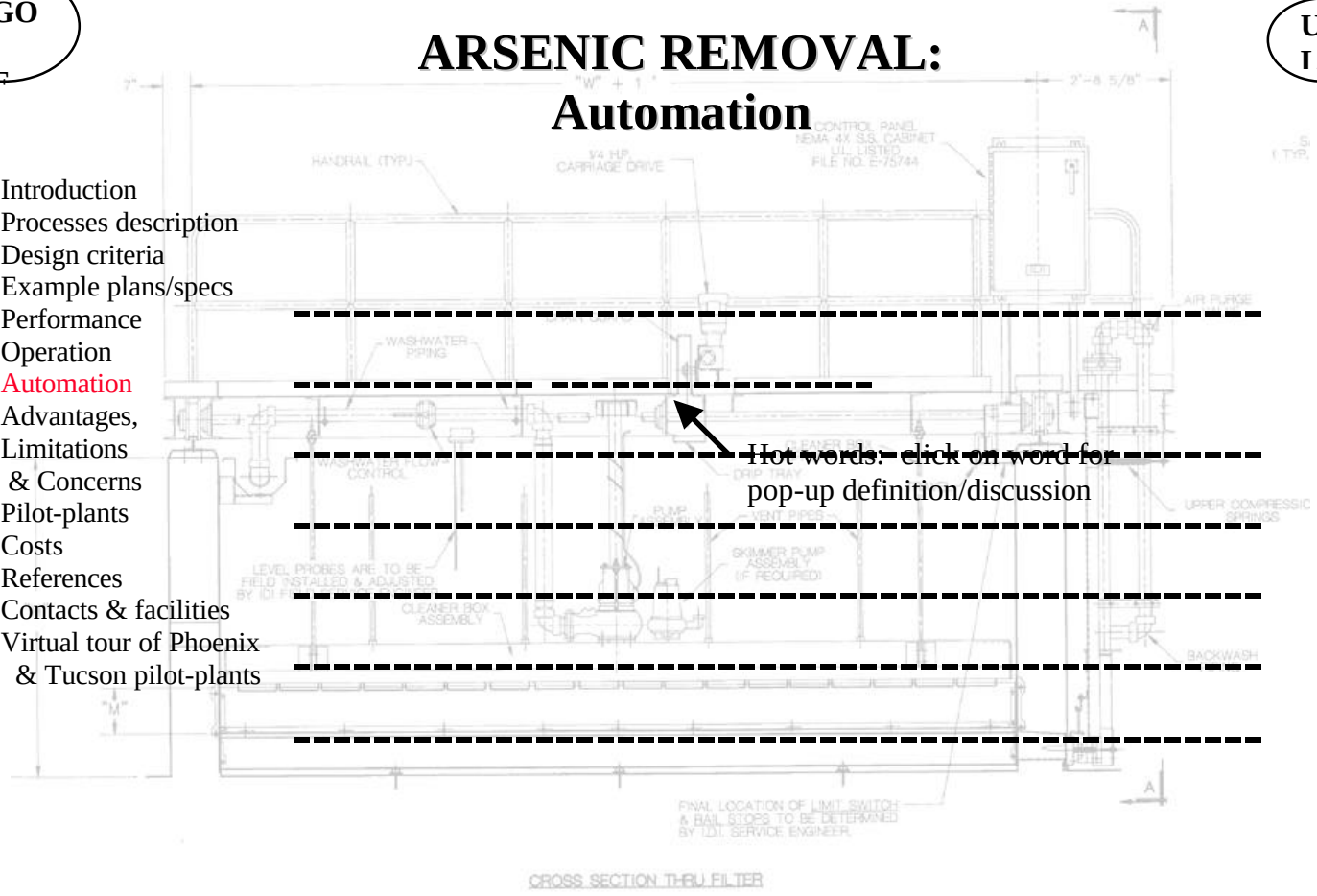
- Contacts & facilities
- Virtual tour of Phoenix & Tucson pilot-plants

Hot words: click on word for pop-up definition/discussion



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UTK LOG

ARSENIC REMOVAL:
Advantages, limitations and concerns

- Introduction
- Processes description
- Design criteria
- Example plans/specs
- Performance
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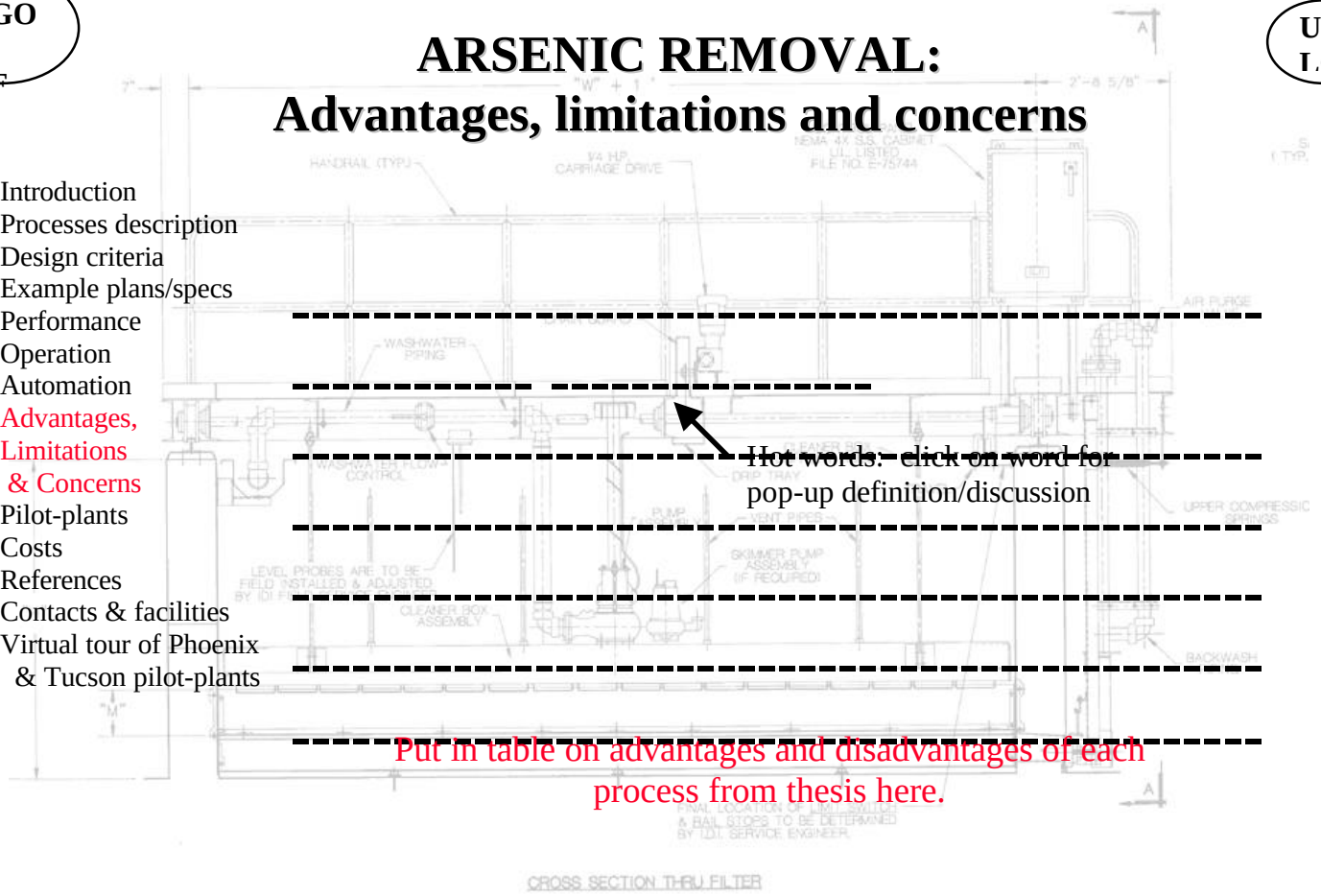
- Automation
- Advantages, Limitations & Concerns
- Pilot-plants
- Costs
- References
- Contacts & facilities
- Virtual tour of Phoenix & Tucson pilot-plants

Hot words: click on word for pop-up definition/discussion

Put in table on advantages and disadvantages of each process from thesis here.



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Pilot-Plants

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- Processes description
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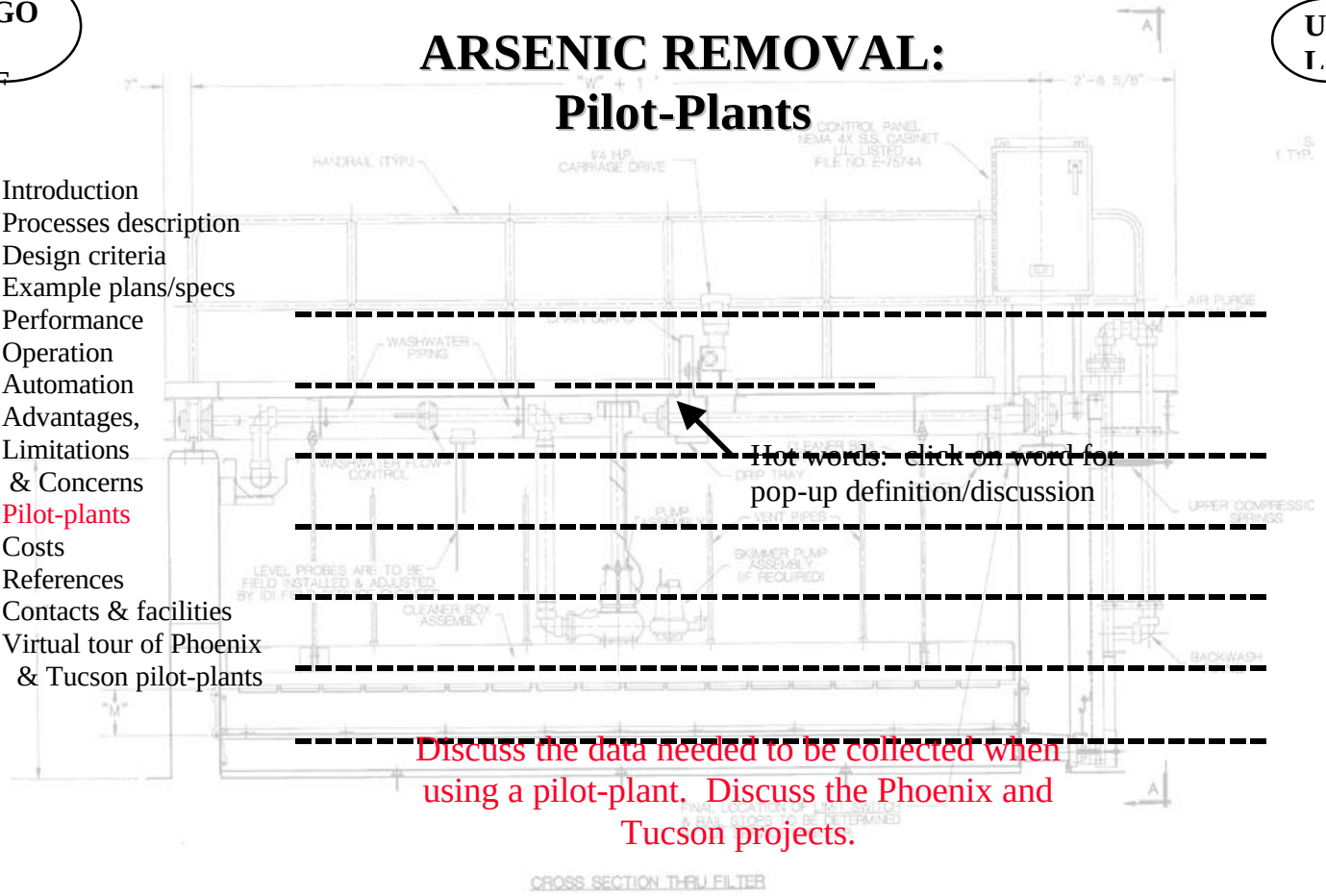
- Advantages, Limitations & Concerns
- Pilot-plants
- Costs
- References
- Contacts & facilities
- Virtual tour of Phoenix & Tucson pilot-plants

Hot words: click on word for pop-up definition/discussion

Discuss the data needed to be collected when using a pilot-plant. Discuss the Phoenix and Tucson projects.



BACK NEXT EXIT

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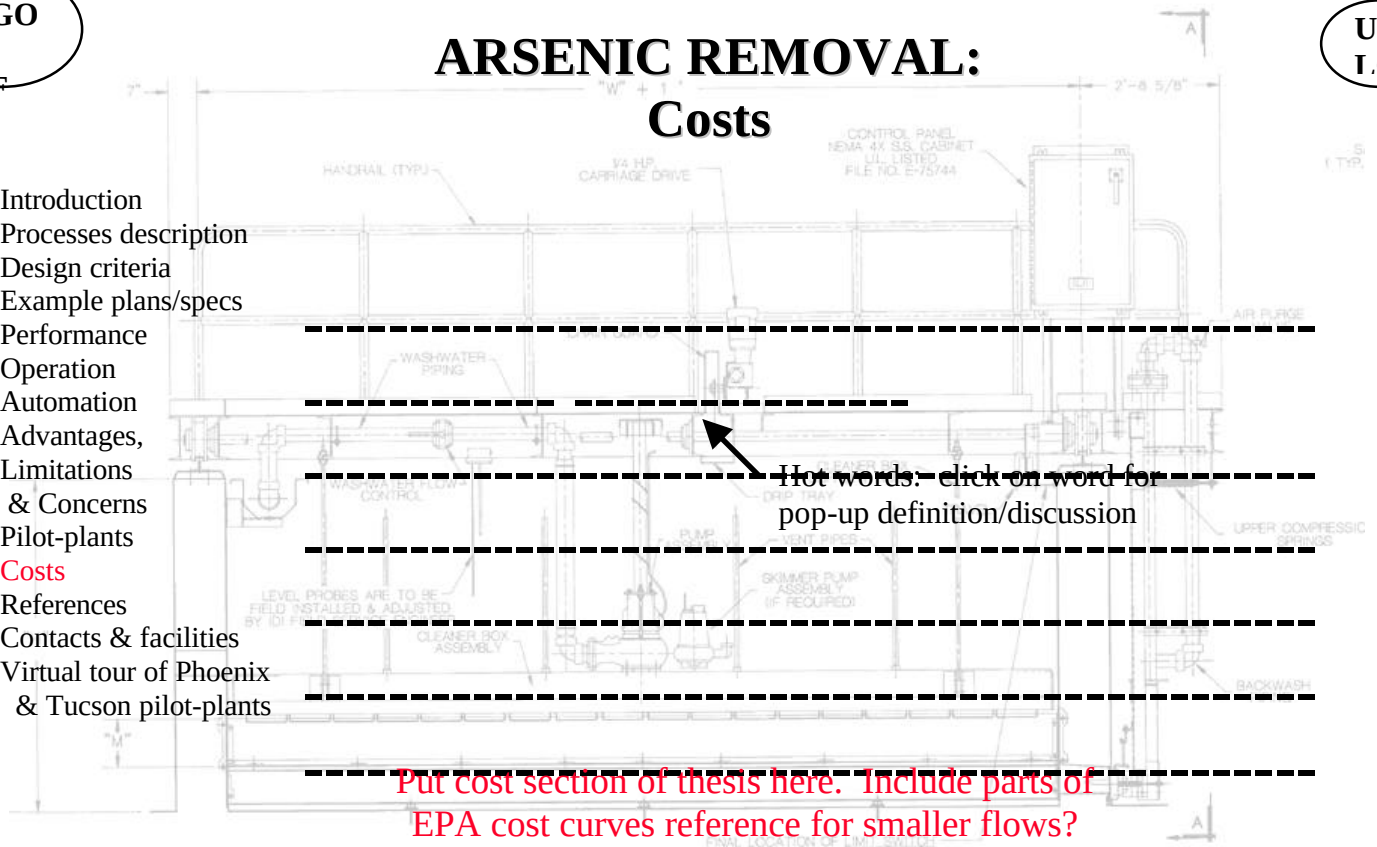
UTK LOG

ARSENIC REMOVAL:
Costs



- Introduction
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- Pilot-plants
- Costs
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Hot words: click on word for pop-up definition/discussion

Put cost section of thesis here. Include parts of EPA cost curves reference for smaller flows? Link to table showing costs for each technology for a particular size design flow (1mgd?).

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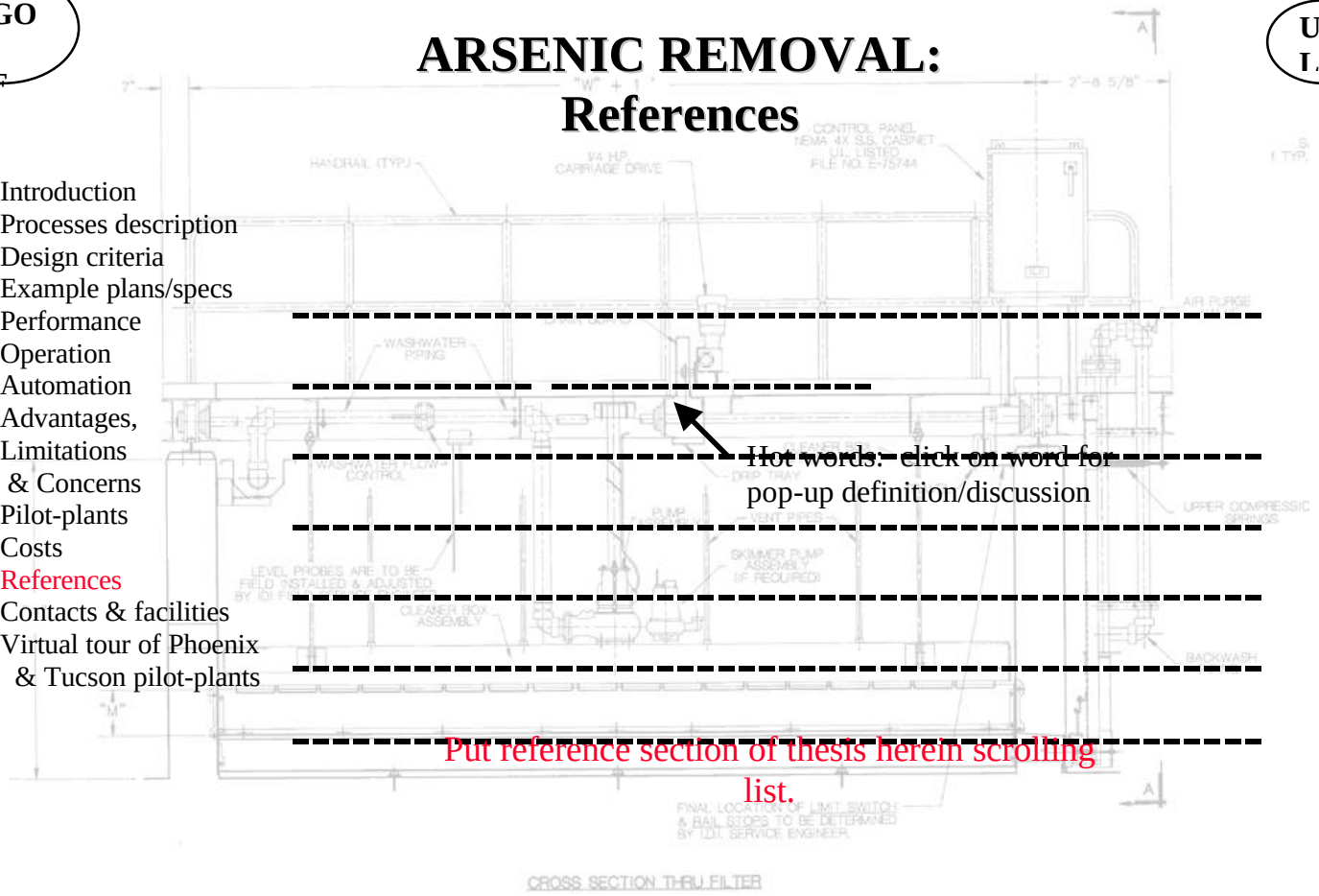
Put reference section of thesis herein scrolling list.



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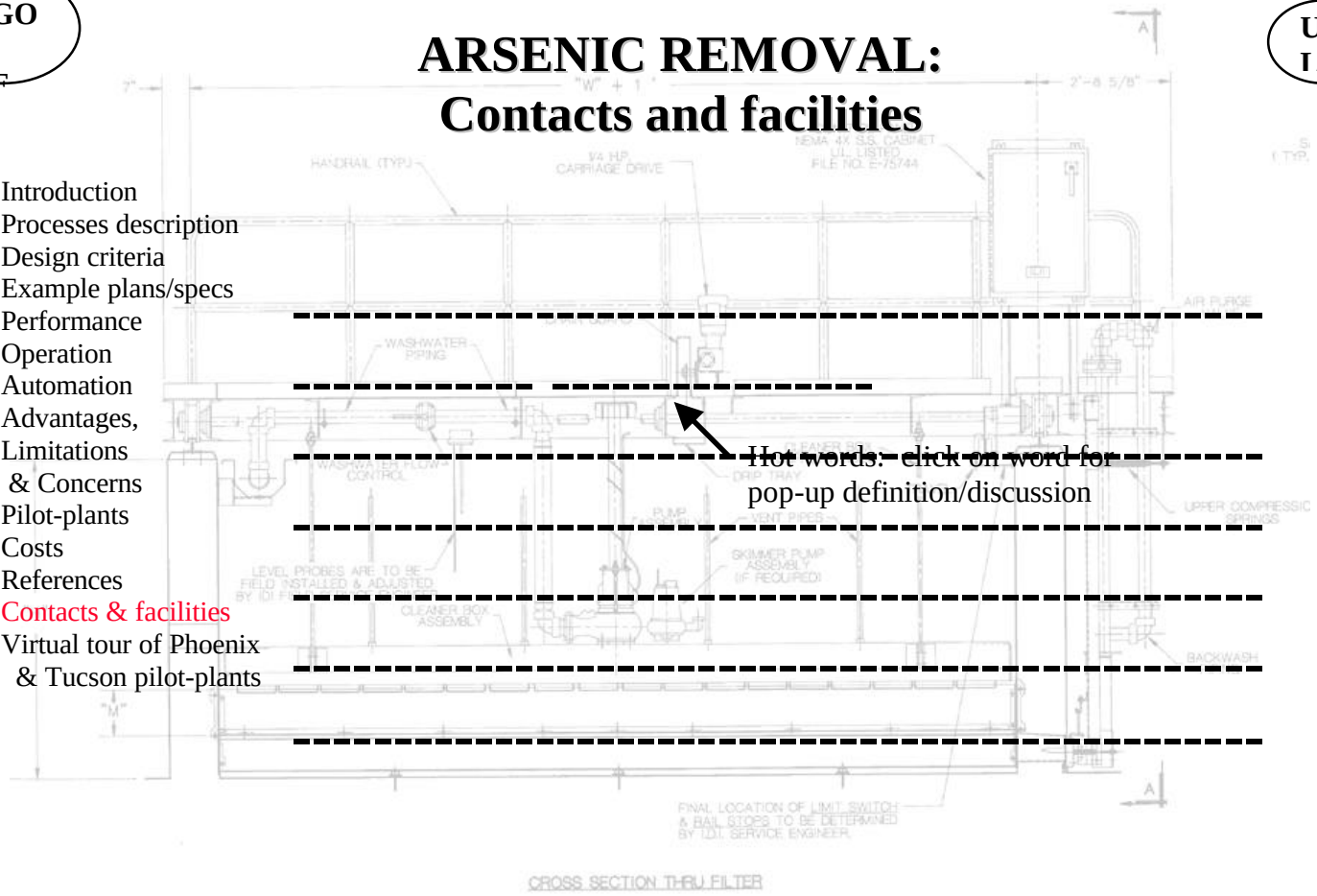
ARSENIC REMOVAL:
Contacts and facilities



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ARSENIC REMOVAL:
Virtual tour of Phoenix & Tucson pilot-plants

- Introduction
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- Costs
- References
- Contacts & facilities

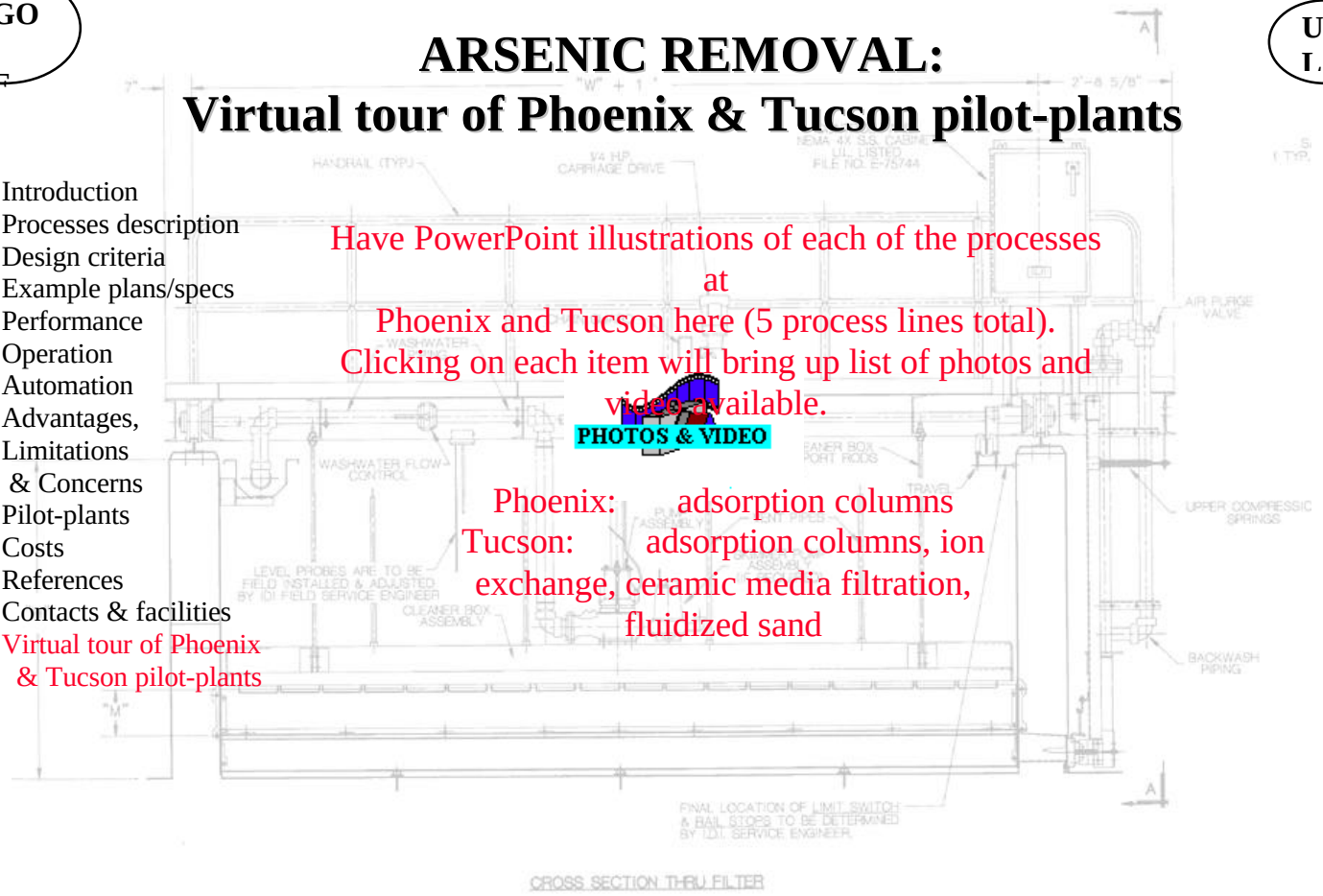
Virtual tour of Phoenix & Tucson pilot-plants

Have PowerPoint illustrations of each of the processes at Phoenix and Tucson here (5 process lines total). Clicking on each item will bring up list of photos and video available.

PHOTOS & VIDEO

Phoenix: adsorption columns

Tucson: adsorption columns, ion exchange, ceramic media filtration, fluidized sand



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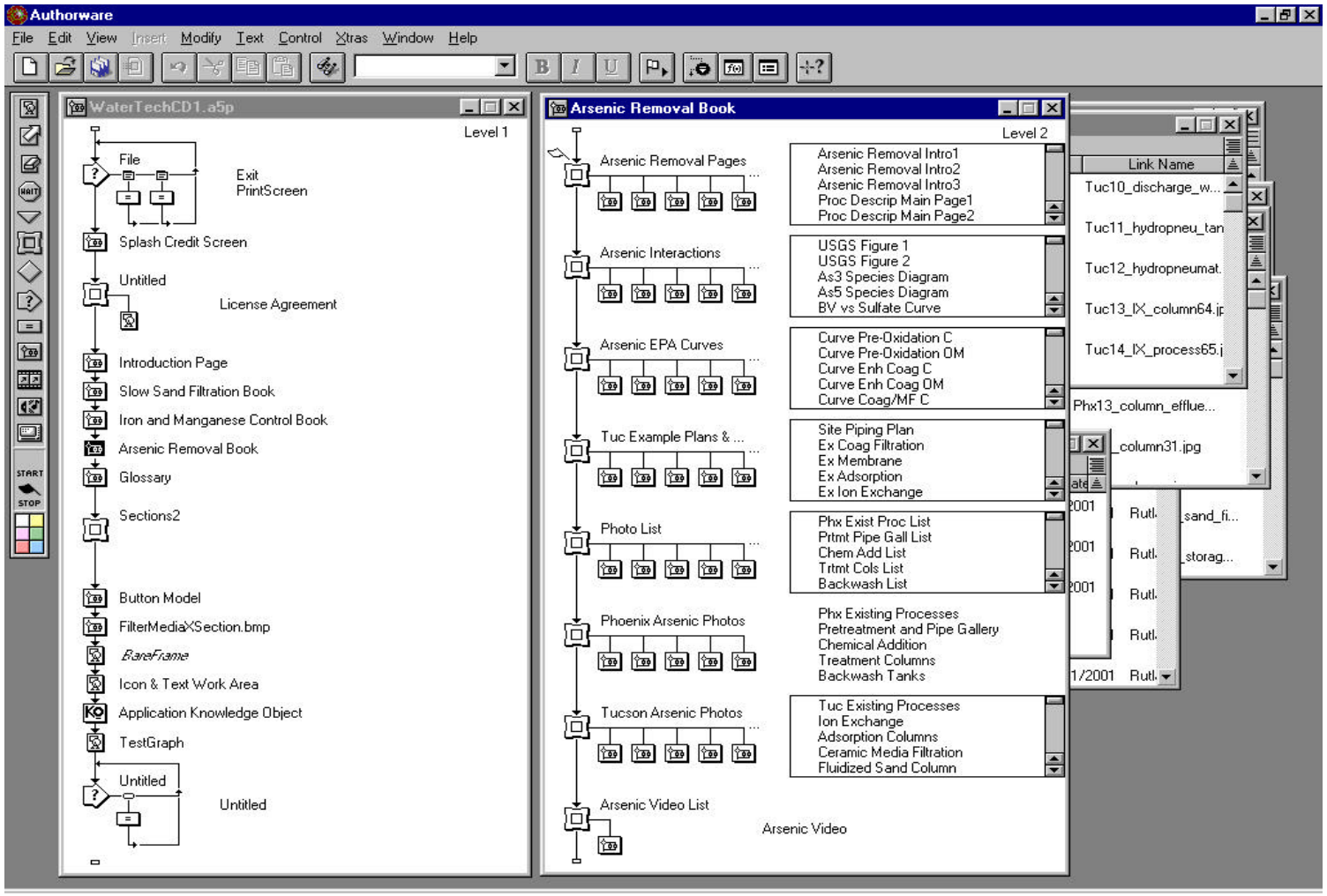
APPENDIX F

SAMPLE AUTHORWARE PROGRAM SCREENS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Icon & Text Work Area
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TestGraph
Untitled
Untitled
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Tuc12_hydropneumat...
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Tuc14_IX_process65.j
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_column31.jpg
_sand_fi...
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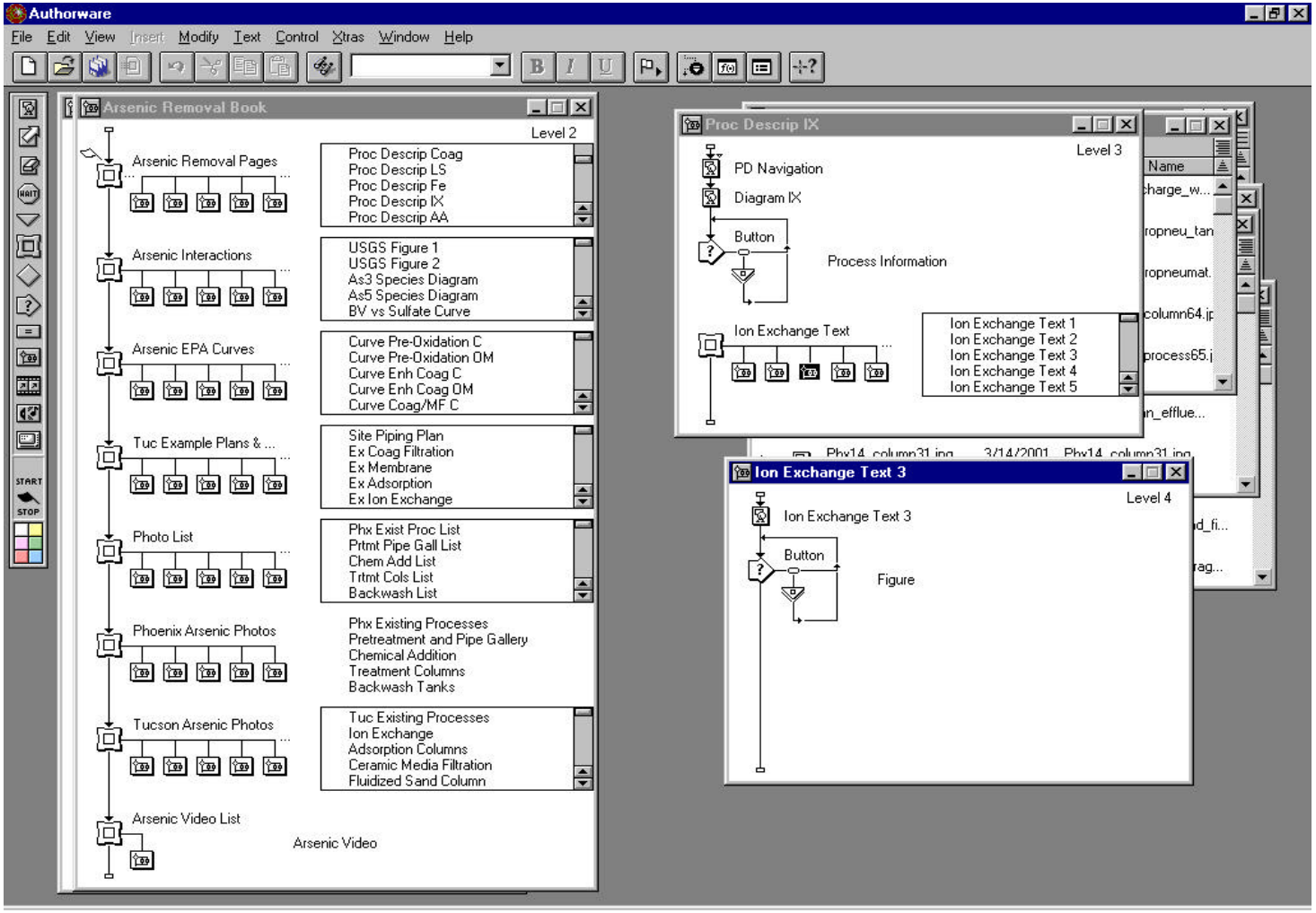
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Proc Descrip LS
Proc Descrip Fe
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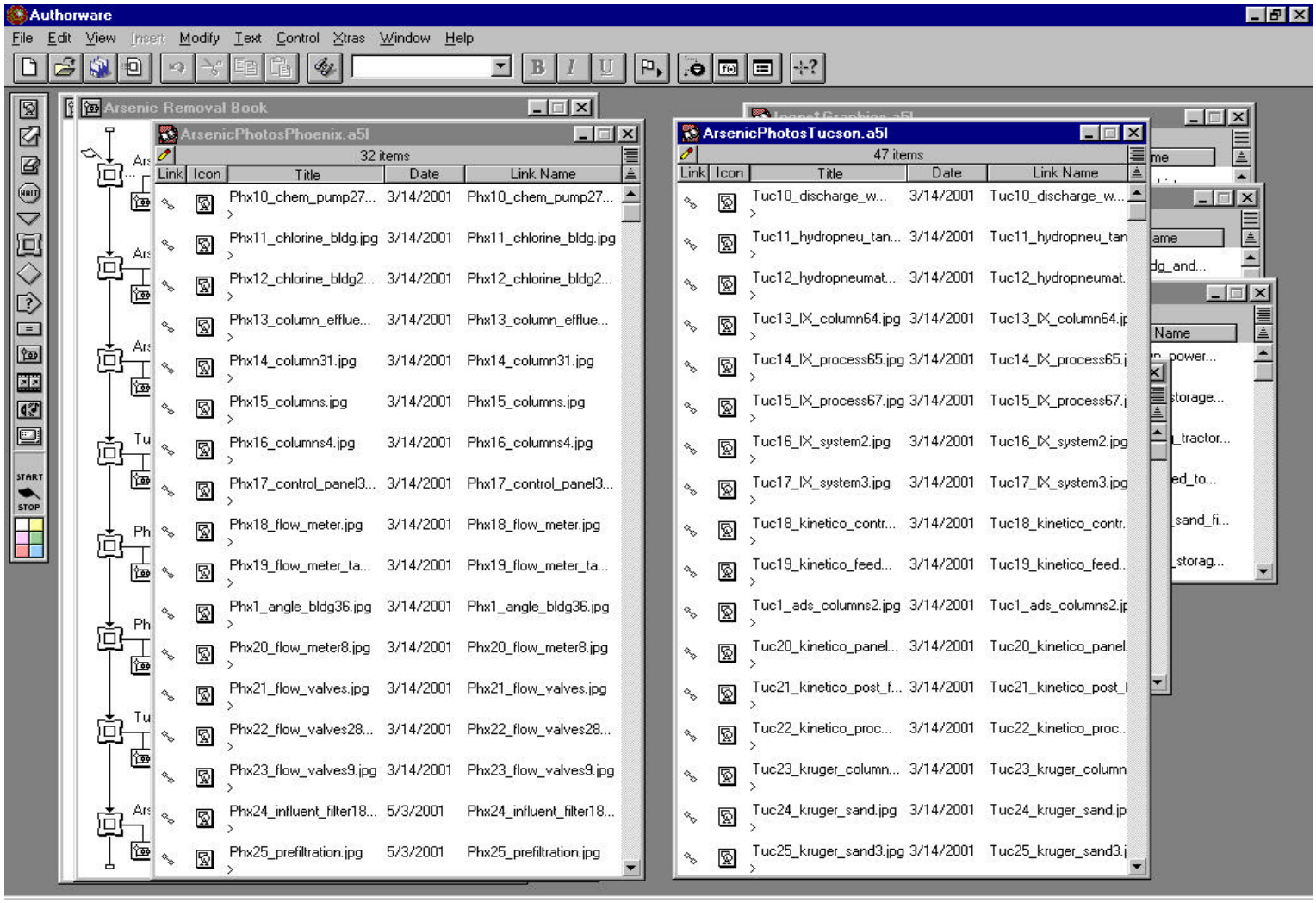
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Phx13_column_efflue... 3/14/2001 Phx13_column_efflue...
Phx14_column31.jpg 3/14/2001 Phx14_column31.jpg
Phx15_columns.jpg 3/14/2001 Phx15_columns.jpg
Phx16_columns4.jpg 3/14/2001 Phx16_columns4.jpg
Phx17_control_panel3... 3/14/2001 Phx17_control_panel3...
Phx18_flow_meter.jpg 3/14/2001 Phx18_flow_meter.jpg
Phx19_flow_meter_ta... 3/14/2001 Phx19_flow_meter_ta...
Phx1_angle_bldg36.jpg 3/14/2001 Phx1_angle_bldg36.jpg
Phx20_flow_meter8.jpg 3/14/2001 Phx20_flow_meter8.jpg
Phx21_flow_valves.jpg 3/14/2001 Phx21_flow_valves.jpg
Phx22_flow_valves28... 3/14/2001 Phx22_flow_valves28...
Phx23_flow_valves9.jpg 3/14/2001 Phx23_flow_valves9.jpg
Phx24_influent_filter18... 5/3/2001 Phx24_influent_filter18...
Phx25_prefiltration.jpg 5/3/2001 Phx25_prefiltration.jpg
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Tuc21_kinetico_post_f... 3/14/2001 Tuc21_kinetico_post_
Tuc22_kinetico_proc... 3/14/2001 Tuc22_kinetico_proc..
Tuc23_kruger_column... 3/14/2001 Tuc23_kruger_column
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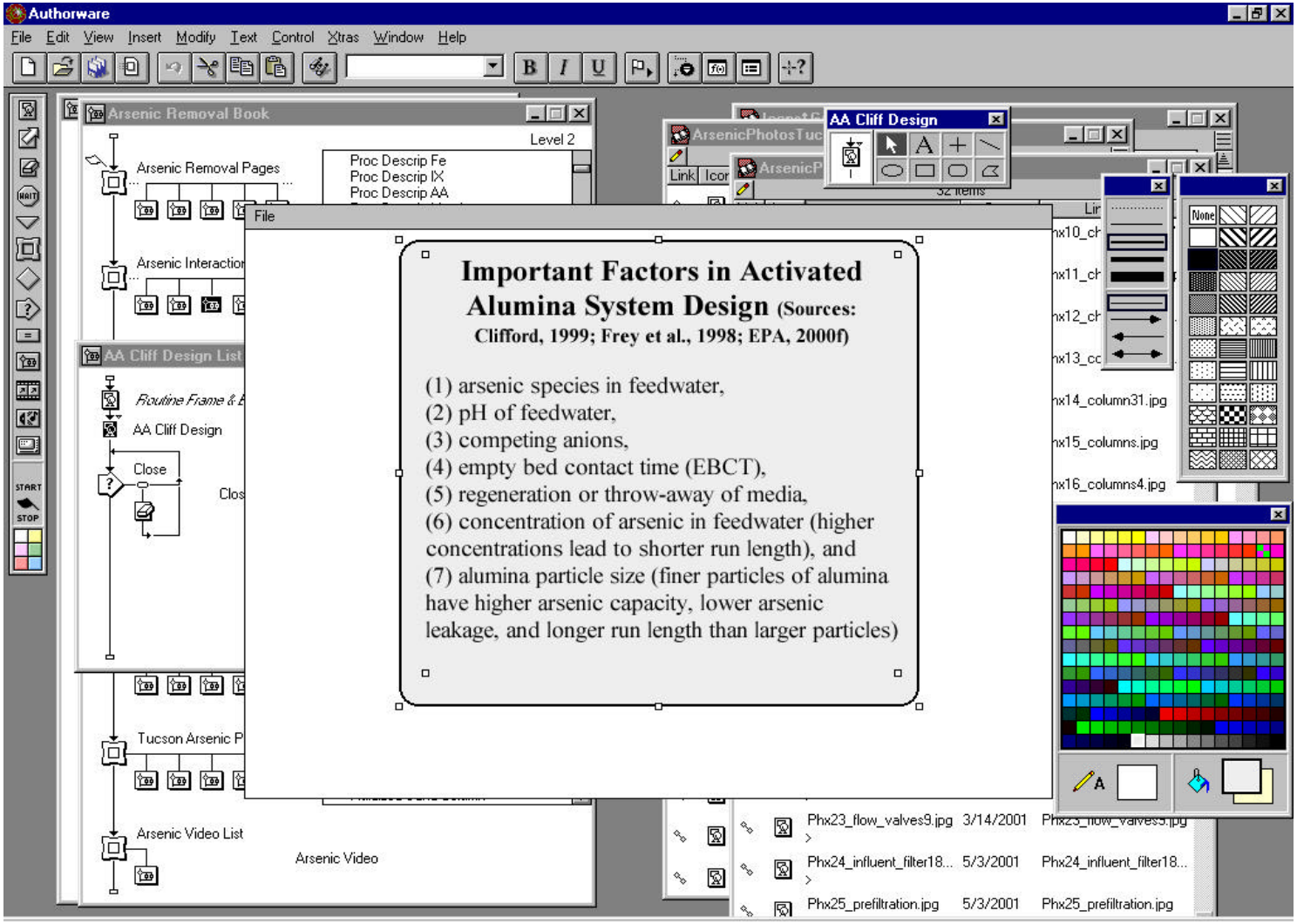
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Proc Descrip IX
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Routine Frame & E
AA Cliff Design
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Tucson Arsenic P
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File
Important Factors in Activated Alumina System Design (Sources: Clifford, 1999; Frey et al., 1998; EPA, 2000f)
(1) arsenic species in feedwater,
(2) pH of feedwater,
(3) competing anions,
(4) empty bed contact time (EBCT),
(5) regeneration or throw-away of media,
(6) concentration of arsenic in feedwater (higher concentrations lead to shorter run length), and
(7) alumina particle size (finer particles of alumina have higher arsenic capacity, lower arsenic leakage, and longer run length than larger particles)
Phx23_flow_valves9.jpg 3/14/2001
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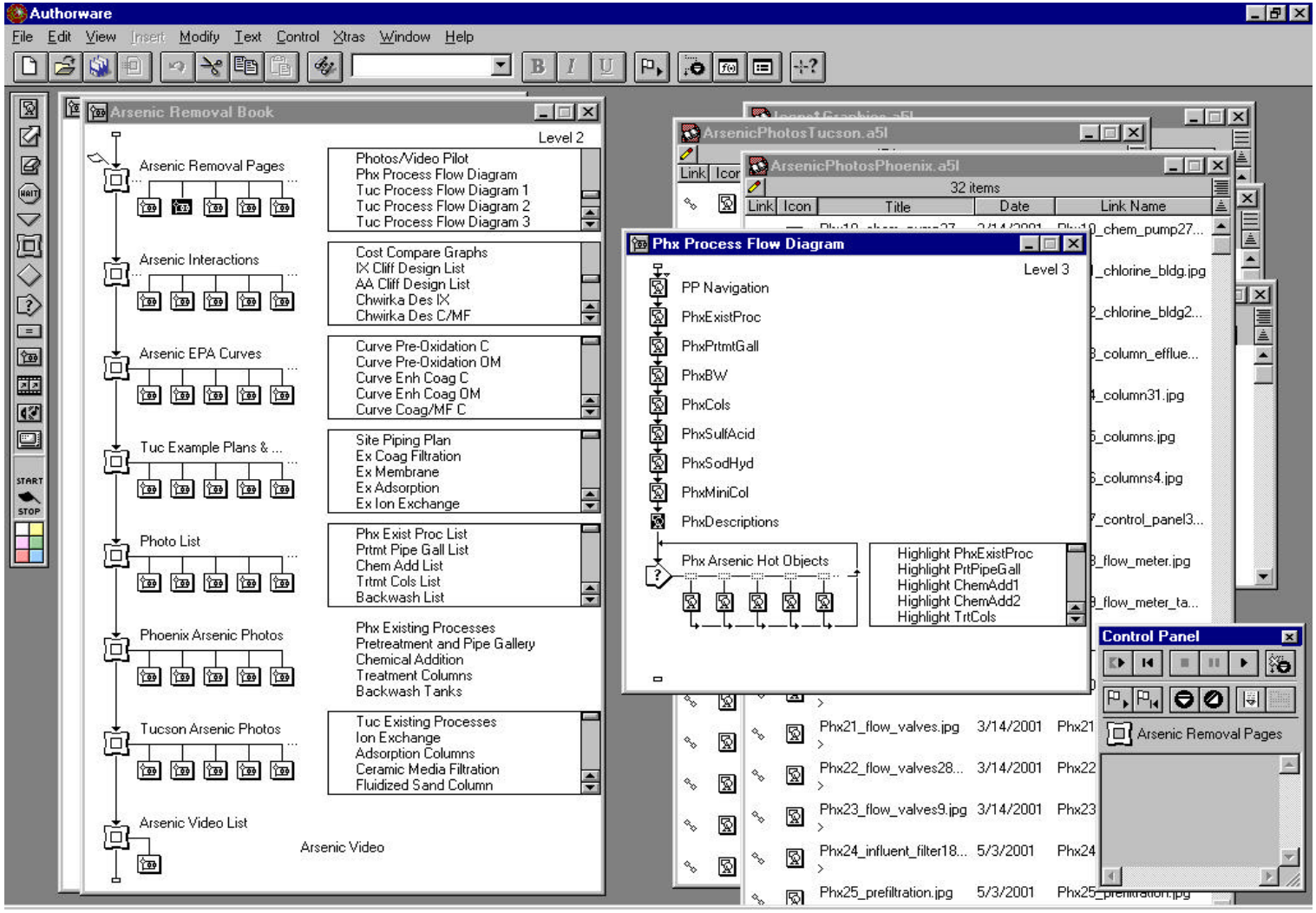
Phx25_prefiltration.jpg 5/3/2001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Highlight ChemAdd2
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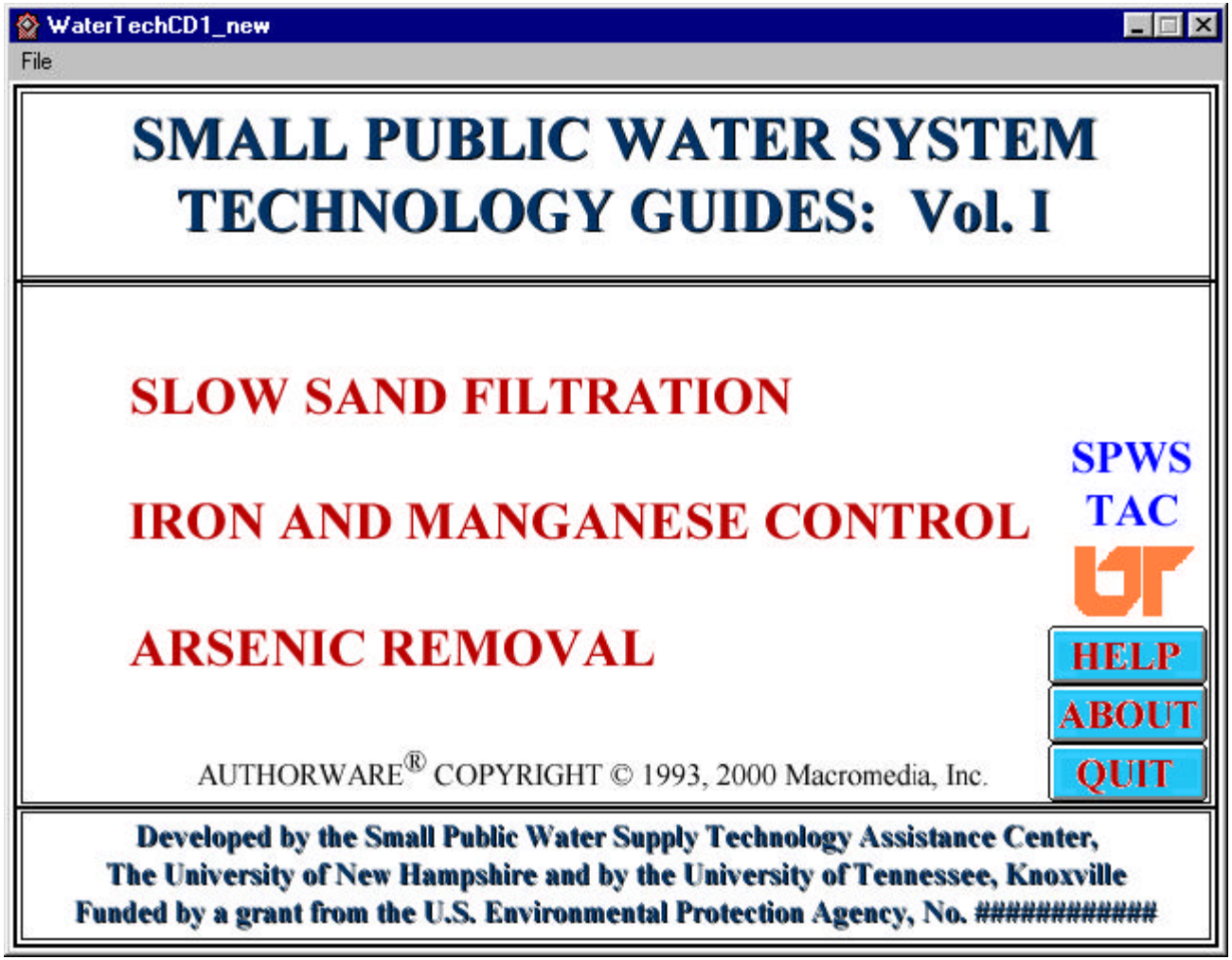
Phx25_prefiltration.jpg 5/3/2001

APPENDIX G

ARSENIC MODULE SCREEN CAPTURES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SMALL PUBLIC WATER SYSTEM TECHNOLOGY GUIDES: Vol. I
SLOW SAND FILTRATION
IRON AND MANGANESE CONTROL
ARSENIC REMOVAL
SPWS
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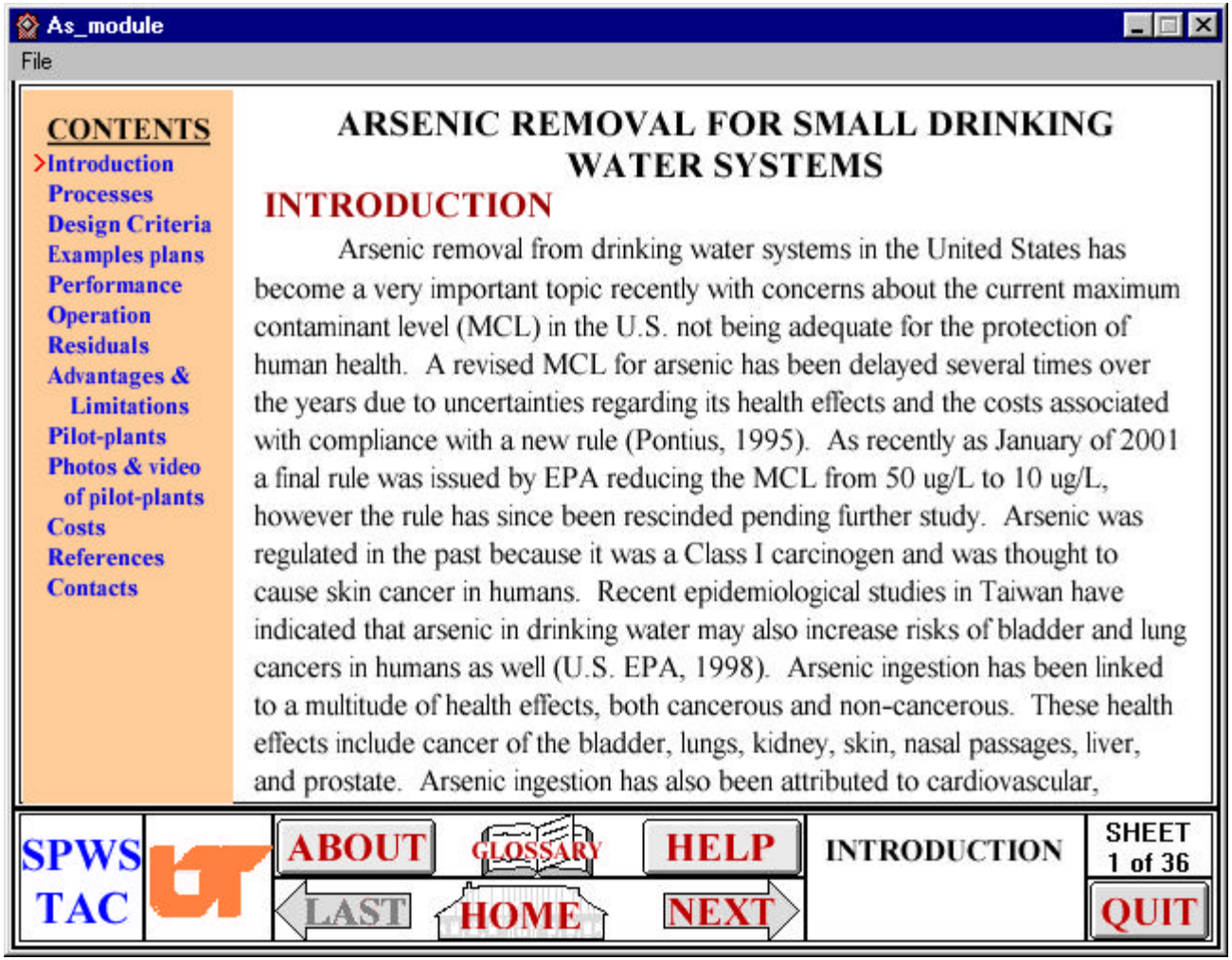
Developed by the Small Public Water Supply Technology Assistance Center,
The University of New Hampshire and by the University of Tennessee, Knoxville
Funded by a grant from the U.S. Environmental Protection Agency, No. ##########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ARSENIC REMOVAL FOR SMALL DRINKING WATER SYSTEMS
INTRODUCTION
Arsenic removal from drinking water systems in the United States has become a very important topic recently with concerns about the current maximum contaminant level (MCL) in the U.S. not being adequate for the protection of human health. A revised MCL for arsenic has been delayed several times over the years due to uncertainties regarding its health effects and the costs associated with compliance with a new rule (Pontius, 1995). As recently as January of 2001 a final rule was issued by EPA reducing the MCL from 50 ug/L to 10 ug/L, however the rule has since been rescinded pending further study. Arsenic was regulated in the past because it was a Class I carcinogen and was thought to cause skin cancer in humans. Recent epidemiological studies in Taiwan have indicated that arsenic in drinking water may also increase risks of bladder and lung cancers in humans as well (U.S. EPA, 1998). Arsenic ingestion has been linked to a multitude of health effects, both cancerous and non-cancerous. These health effects include cancer of the bladder, lungs, kidney, skin, nasal passages, liver, and prostate. Arsenic ingestion has also been attributed to cardiovascular,
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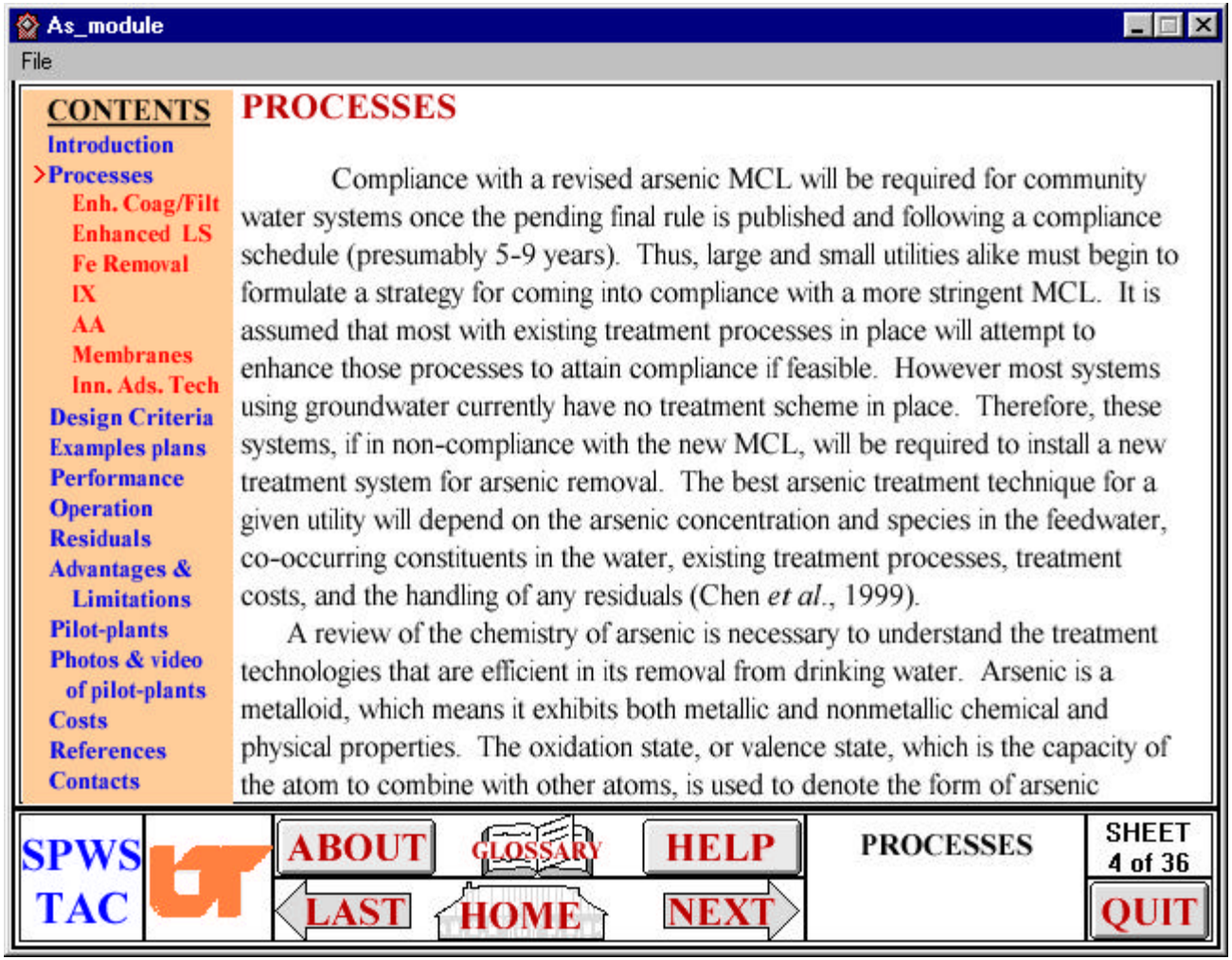
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Compliance with a revised arsenic MCL will be required for community water systems once the pending final rule is published and following a compliance schedule (presumably 5-9 years). Thus, large and small utilities alike must begin to formulate a strategy for coming into compliance with a more stringent MCL. It is assumed that most with existing treatment processes in place will attempt to enhance those processes to attain compliance if feasible. However most systems using groundwater currently have no treatment scheme in place. Therefore, these systems, if in non-compliance with the new MCL, will be required to install a new treatment system for arsenic removal. The best arsenic treatment technique for a given utility will depend on the arsenic concentration and species in the feedwater, co-occurring constituents in the water, existing treatment processes, treatment costs, and the handling of any residuals (Chen et al., 1999).
A review of the chemistry of arsenic is necessary to understand the treatment technologies that are efficient in its removal from drinking water. Arsenic is a metalloid, which means it exhibits both metallic and nonmetallic chemical and physical properties. The oxidation state, or valence state, which is the capacity of the atom to combine with other atoms, is used to denote the form of arsenic
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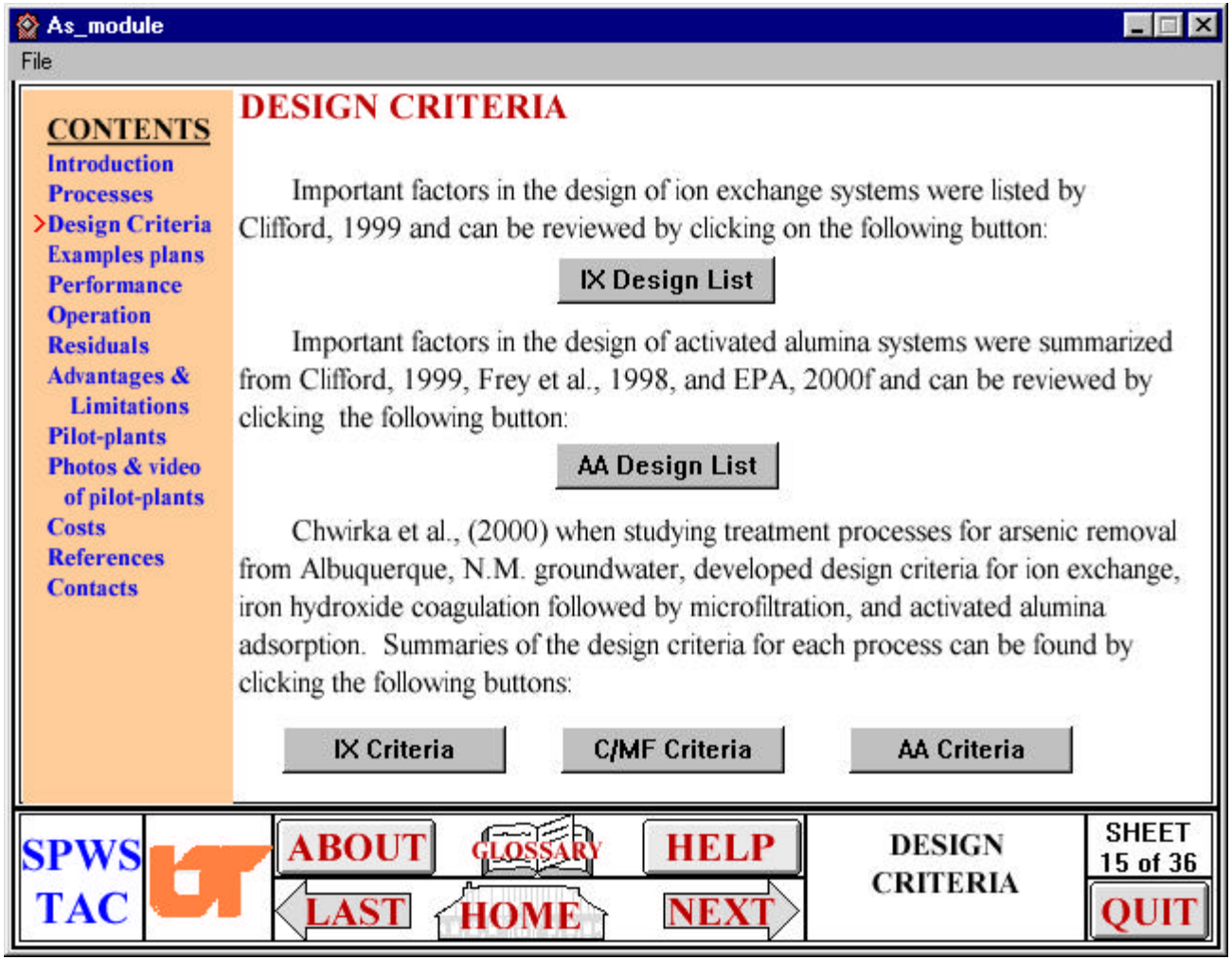
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DESIGN CRITERIA
Important factors in the design of ion exchange systems were listed by Clifford, 1999 and can be reviewed by clicking on the following button:
IX Design List
Important factors in the design of activated alumina systems were summarized from Clifford, 1999, Frey et al., 1998, and EPA, 2000f and can be reviewed by clicking the following button:
AA Design List
Chwirka et al., (2000) when studying treatment processes for arsenic removal from Albuquerque, N.M. groundwater, developed design criteria for ion exchange, iron hydroxide coagulation followed by microfiltration, and activated alumina adsorption. Summaries of the design criteria for each process can be found by clicking the following buttons:
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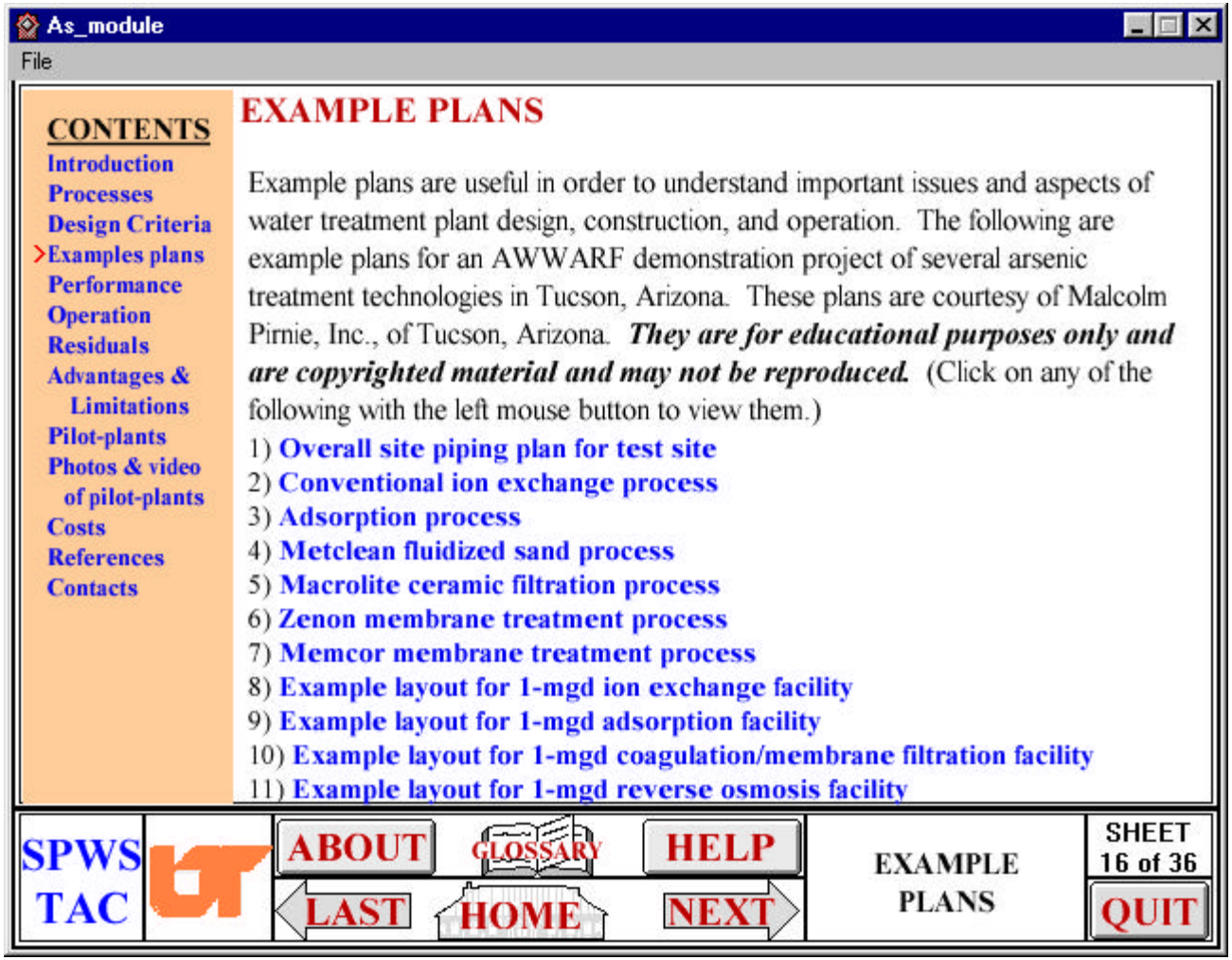
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EXAMPLE PLANS
Example plans are useful in order to understand important issues and aspects of water treatment plant design, construction, and operation. The following are example plans for an AWWARF demonstration project of several arsenic treatment technologies in Tucson, Arizona. These plans are courtesy of Malcolm Pirnie, Inc., of Tucson, Arizona. They are for educational purposes only and are copyrighted material and may not be reproduced. (Click on any of the following with the left mouse button to view them.)
1) Overall site piping plan for test site
2) Conventional ion exchange process
3) Adsorption process
4) Metclean fluidized sand process
5) Macrolite ceramic filtration process
6) Zenon membrane treatment process
7) Memcor membrane treatment process
8) Example layout for 1-mgd ion exchange facility
9) Example layout for 1-mgd adsorption facility
10) Example layout for 1-mgd coagulation/membrane filtration facility
11) Example layout for 1-mgd reverse osmosis facility
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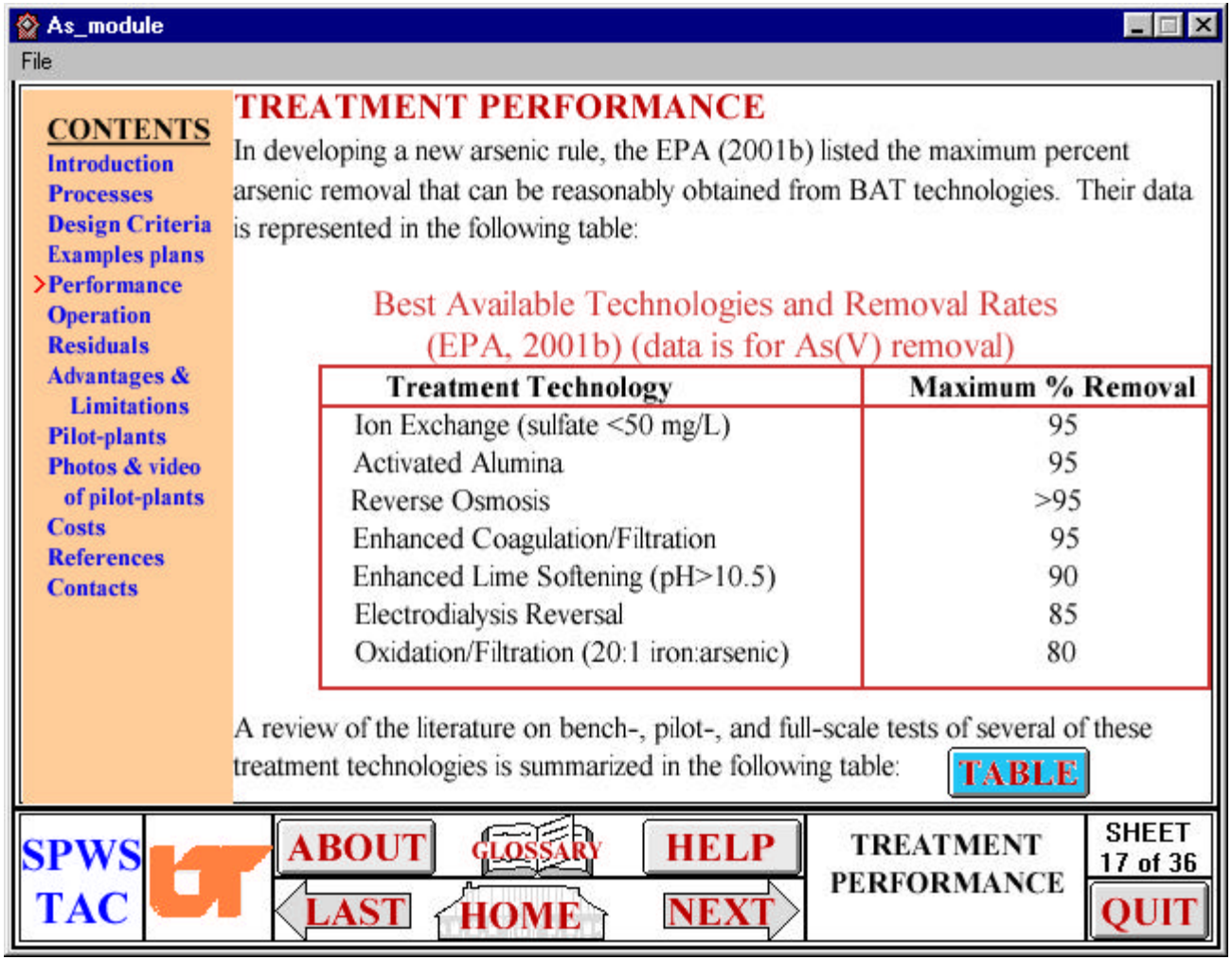
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TREATMENT PERFORMANCE
In developing a new arsenic rule, the EPA (2001b) listed the maximum percent arsenic removal that can be reasonably obtained from BAT technologies. Their data is represented in the following table:
Best Available Technologies and Removal Rates
(EPA, 2001b) (data is for As(V) removal)
Treatment Technology | Maximum % Removal
Ion Exchange (sulfate <50 mg/L) | 95
Activated Alumina | 95
Reverse Osmosis | >95
Enhanced Coagulation/Filtration | 95
Enhanced Lime Softening (pH>10.5) | 90
Electrodialysis Reversal | 85
Oxidation/Filtration (20:1 iron:arsenic) | 80
A review of the literature on bench-, pilot-, and full-scale tests of several of these treatment technologies is summarized in the following table:
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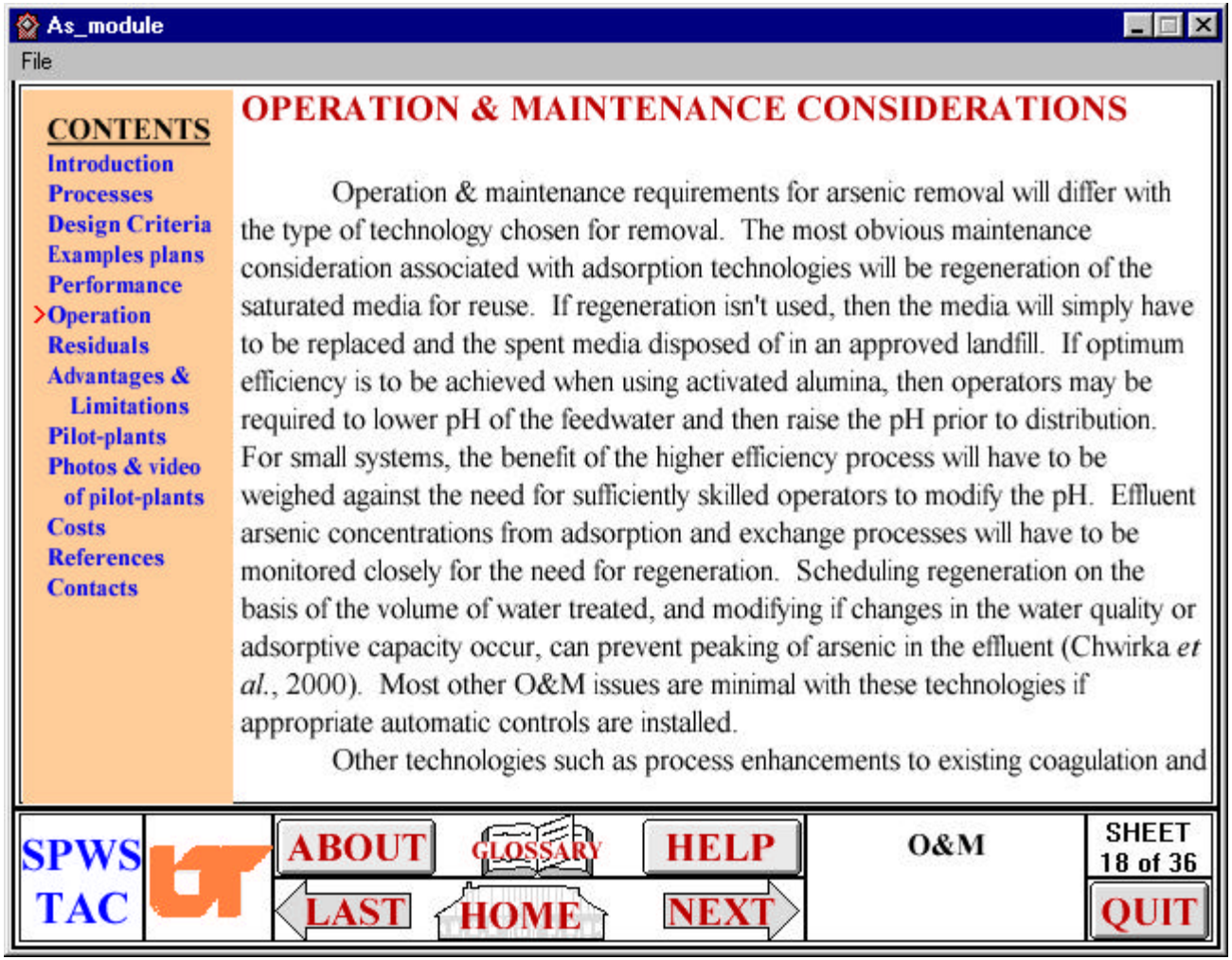
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OPERATION & MAINTENANCE CONSIDERATIONS
Operation & maintenance requirements for arsenic removal will differ with the type of technology chosen for removal. The most obvious maintenance consideration associated with adsorption technologies will be regeneration of the saturated media for reuse. If regeneration isn't used, then the media will simply have to be replaced and the spent media disposed of in an approved landfill. If optimum efficiency is to be achieved when using activated alumina, then operators may be required to lower pH of the feedwater and then raise the pH prior to distribution. For small systems, the benefit of the higher efficiency process will have to be weighed against the need for sufficiently skilled operators to modify the pH. Effluent arsenic concentrations from adsorption and exchange processes will have to be monitored closely for the need for regeneration. Scheduling regeneration on the basis of the volume of water treated, and modifying if changes in the water quality or adsorptive capacity occur, can prevent peaking of arsenic in the effluent (Chwirka et al., 2000). Most other O&M issues are minimal with these technologies if appropriate automatic controls are installed.
Other technologies such as process enhancements to existing coagulation and
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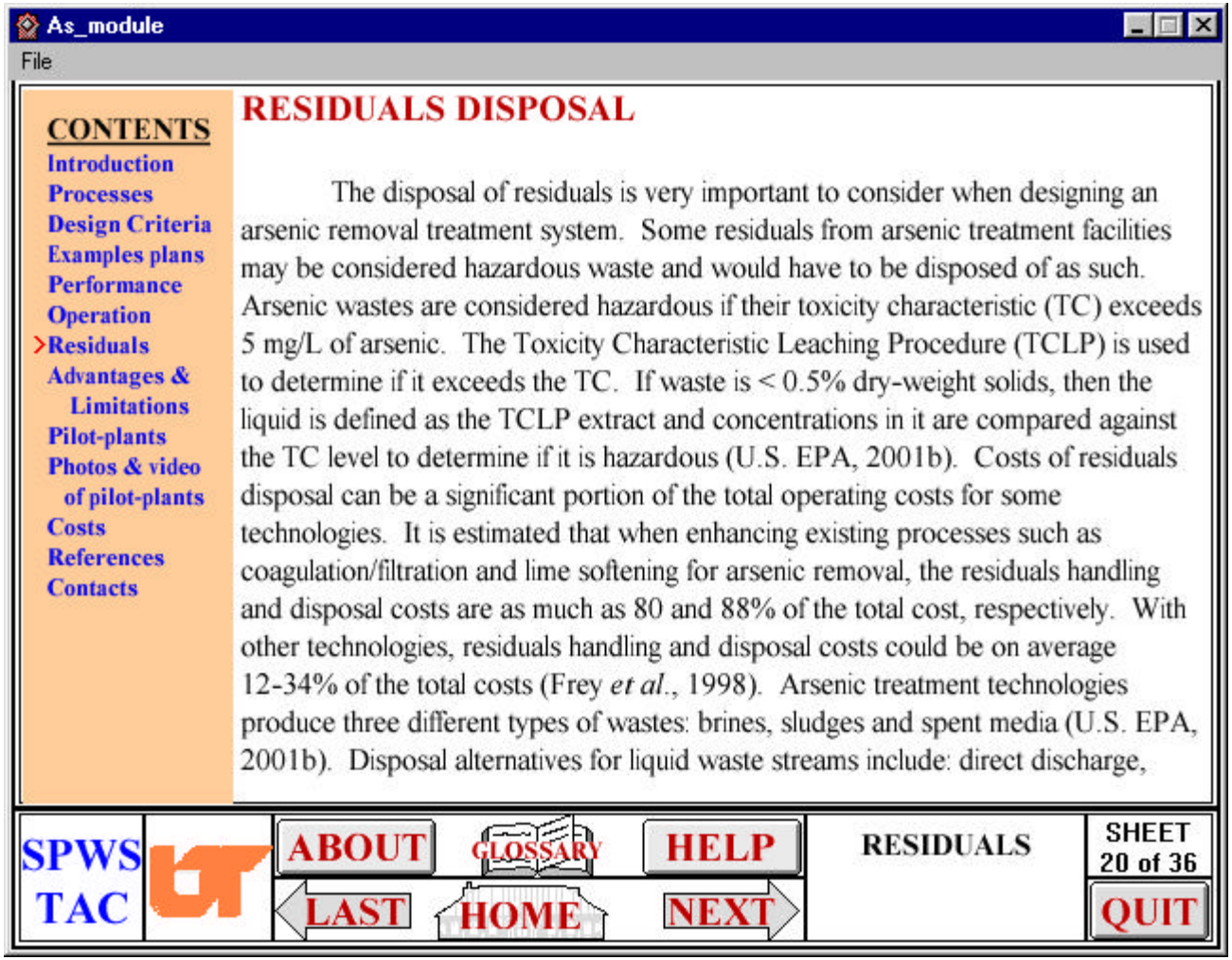
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RESIDUALS DISPOSAL
The disposal of residuals is very important to consider when designing an arsenic removal treatment system. Some residuals from arsenic treatment facilities may be considered hazardous waste and would have to be disposed of as such. Arsenic wastes are considered hazardous if their toxicity characteristic (TC) exceeds 5 mg/L of arsenic. The Toxicity Characteristic Leaching Procedure (TCLP) is used to determine if it exceeds the TC. If waste is < 0.5% dry-weight solids, then the liquid is defined as the TCLP extract and concentrations in it are compared against the TC level to determine if it is hazardous (U.S. EPA, 2001b). Costs of residuals disposal can be a significant portion of the total operating costs for some technologies. It is estimated that when enhancing existing processes such as coagulation/filtration and lime softening for arsenic removal, the residuals handling and disposal costs are as much as 80 and 88% of the total cost, respectively. With other technologies, residuals handling and disposal costs could be on average 12-34% of the total costs (Frey et al., 1998). Arsenic treatment technologies produce three different types of wastes: brines, sludges and spent media (U.S. EPA, 2001b). Disposal alternatives for liquid waste streams include: direct discharge,
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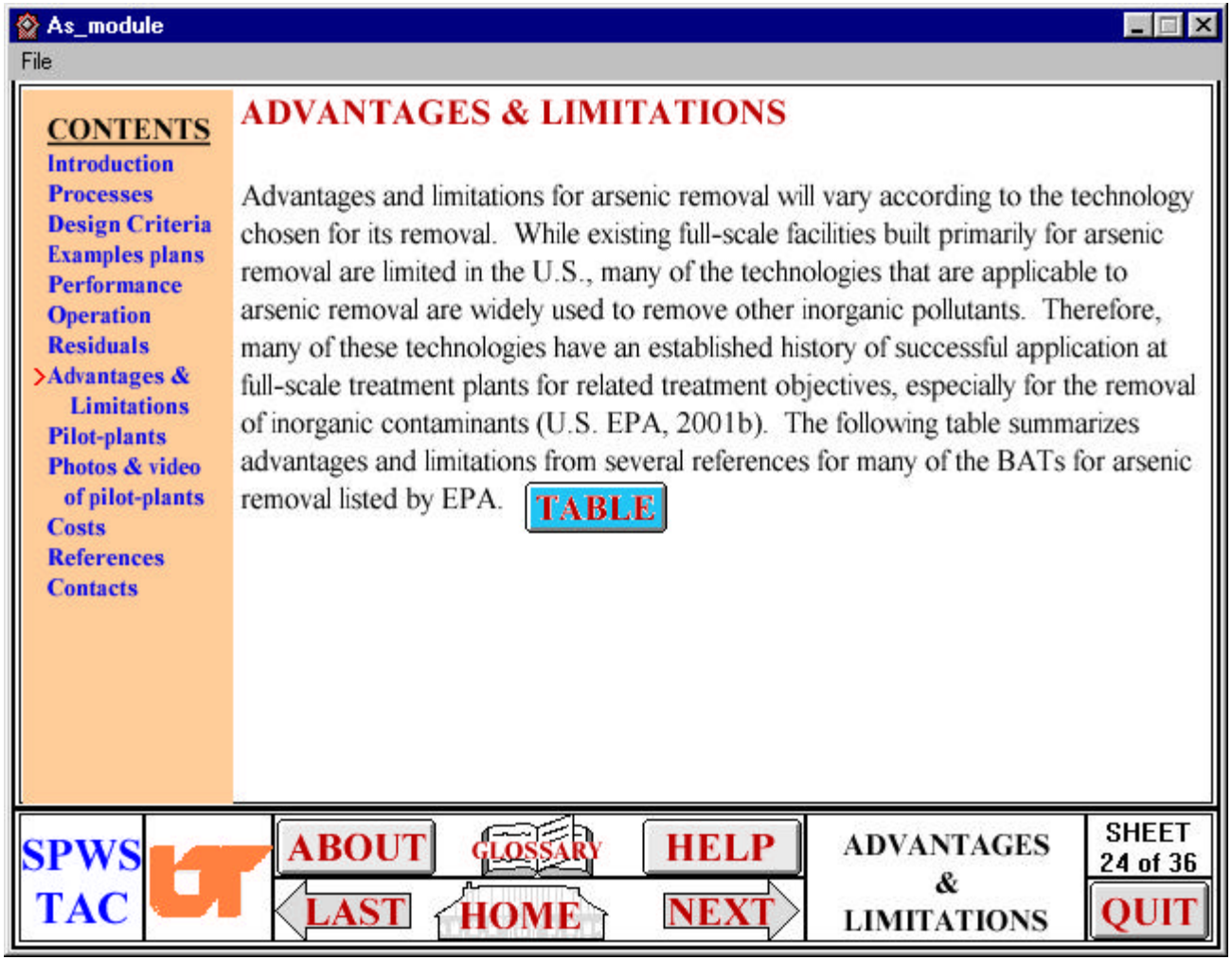
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ADVANTAGES & LIMITATIONS
Advantages and limitations for arsenic removal will vary according to the technology chosen for its removal. While existing full-scale facilities built primarily for arsenic removal are limited in the U.S., many of the technologies that are applicable to arsenic removal are widely used to remove other inorganic pollutants. Therefore, many of these technologies have an established history of successful application at full-scale treatment plants for related treatment objectives, especially for the removal of inorganic contaminants (U.S. EPA, 2001b). The following table summarizes advantages and limitations from several references for many of the BATs for arsenic removal listed by EPA.
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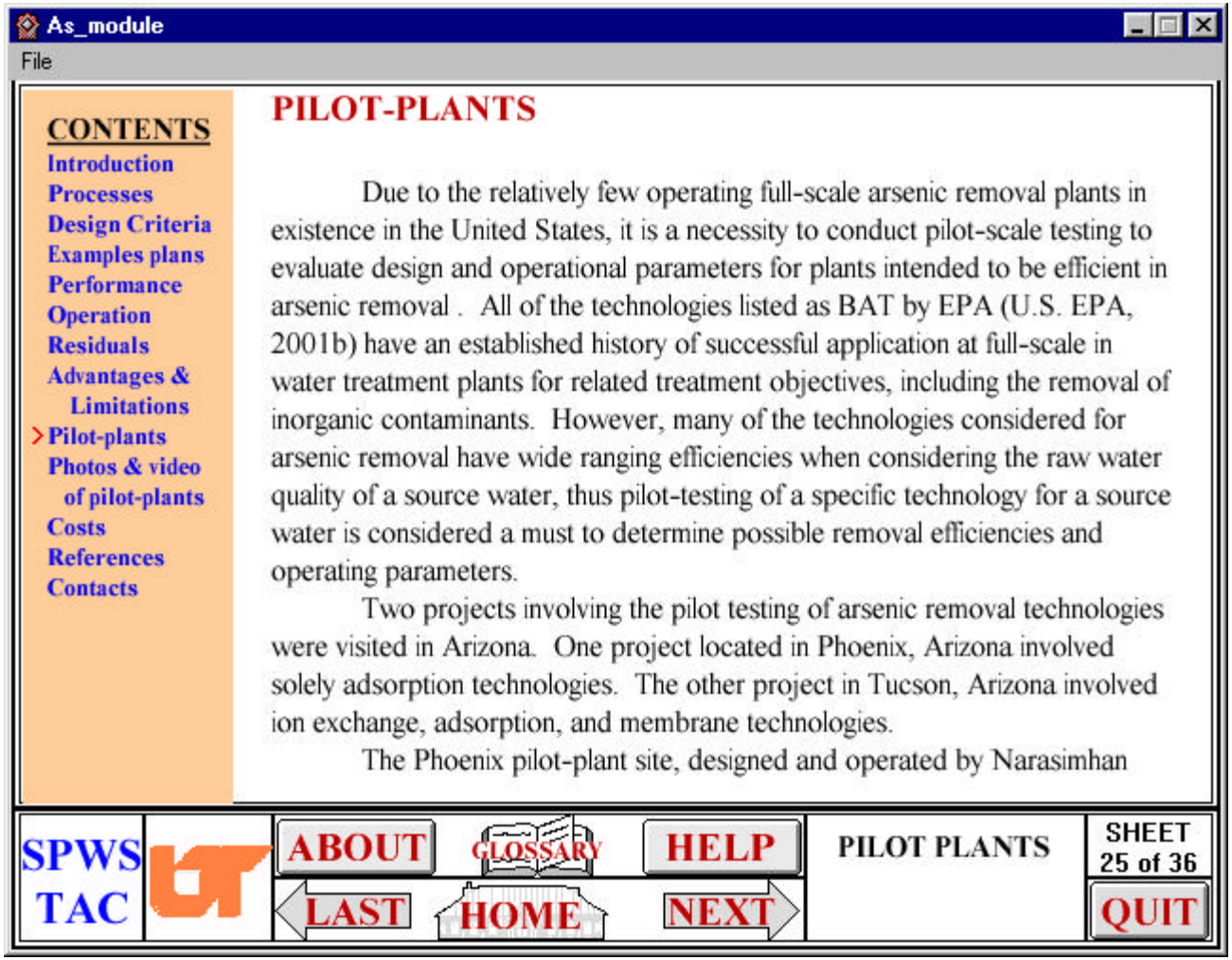
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PILOT-PLANTS
Due to the relatively few operating full-scale arsenic removal plants in existence in the United States, it is a necessity to conduct pilot-scale testing to evaluate design and operational parameters for plants intended to be efficient in arsenic removal . All of the technologies listed as BAT by EPA (U.S. EPA, 2001b) have an established history of successful application at full-scale in water treatment plants for related treatment objectives, including the removal of inorganic contaminants. However, many of the technologies considered for arsenic removal have wide ranging efficiencies when considering the raw water quality of a source water, thus pilot-testing of a specific technology for a source water is considered a must to determine possible removal efficiencies and operating parameters.
Two projects involving the pilot testing of arsenic removal technologies were visited in Arizona. One project located in Phoenix, Arizona involved solely adsorption technologies. The other project in Tucson, Arizona involved ion exchange, adsorption, and membrane technologies.
The Phoenix pilot-plant site, designed and operated by Narasimhan
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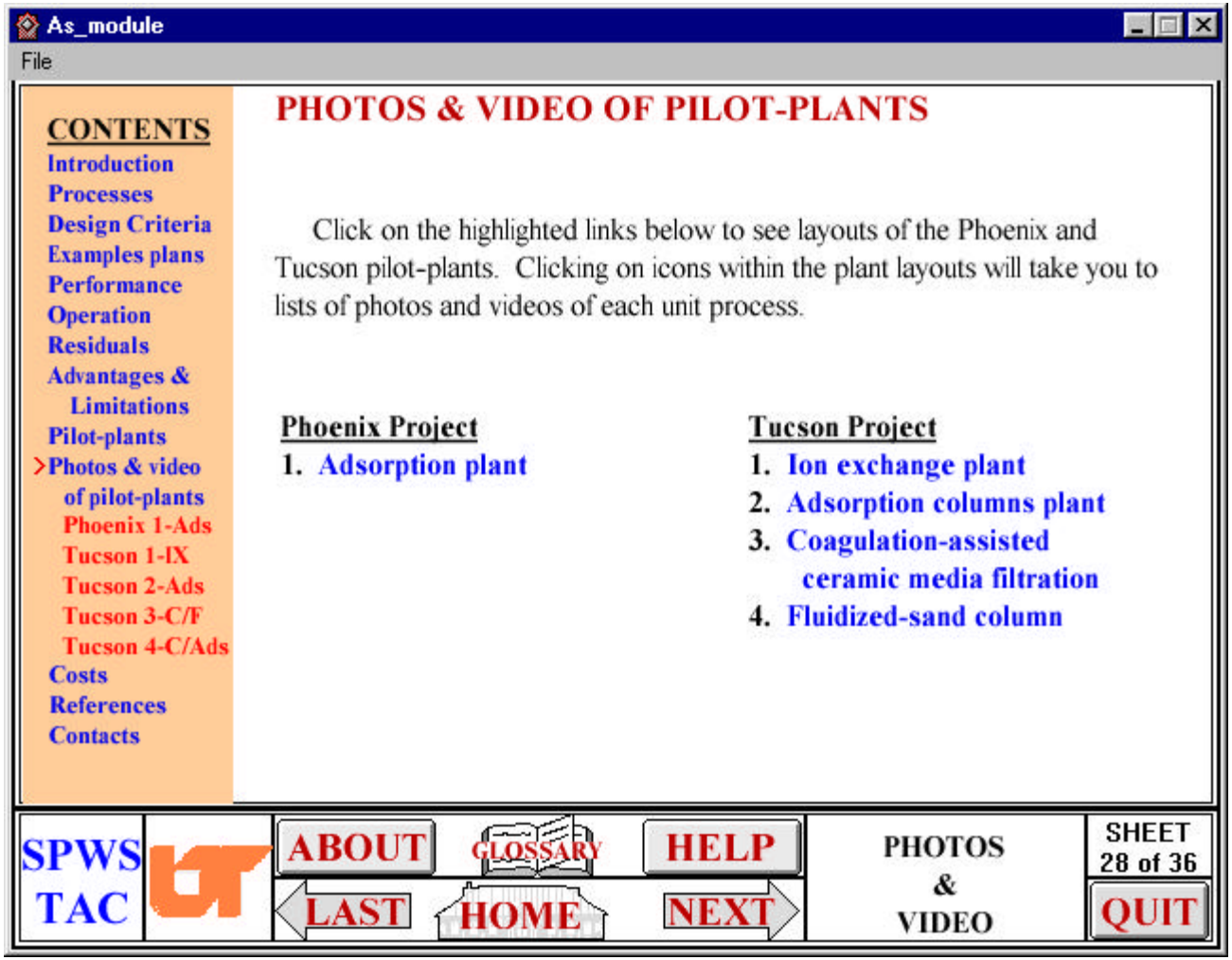
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PHOTOS & VIDEO OF PILOT-PLANTS
Click on the highlighted links below to see layouts of the Phoenix and Tucson pilot-plants. Clicking on icons within the plant layouts will take you to lists of photos and videos of each unit process.
Phoenix Project
1. Adsorption plant
Tucson Project
1. Ion exchange plant
2. Adsorption columns plant
3. Coagulation-assisted ceramic media filtration
4. Fluidized-sand column
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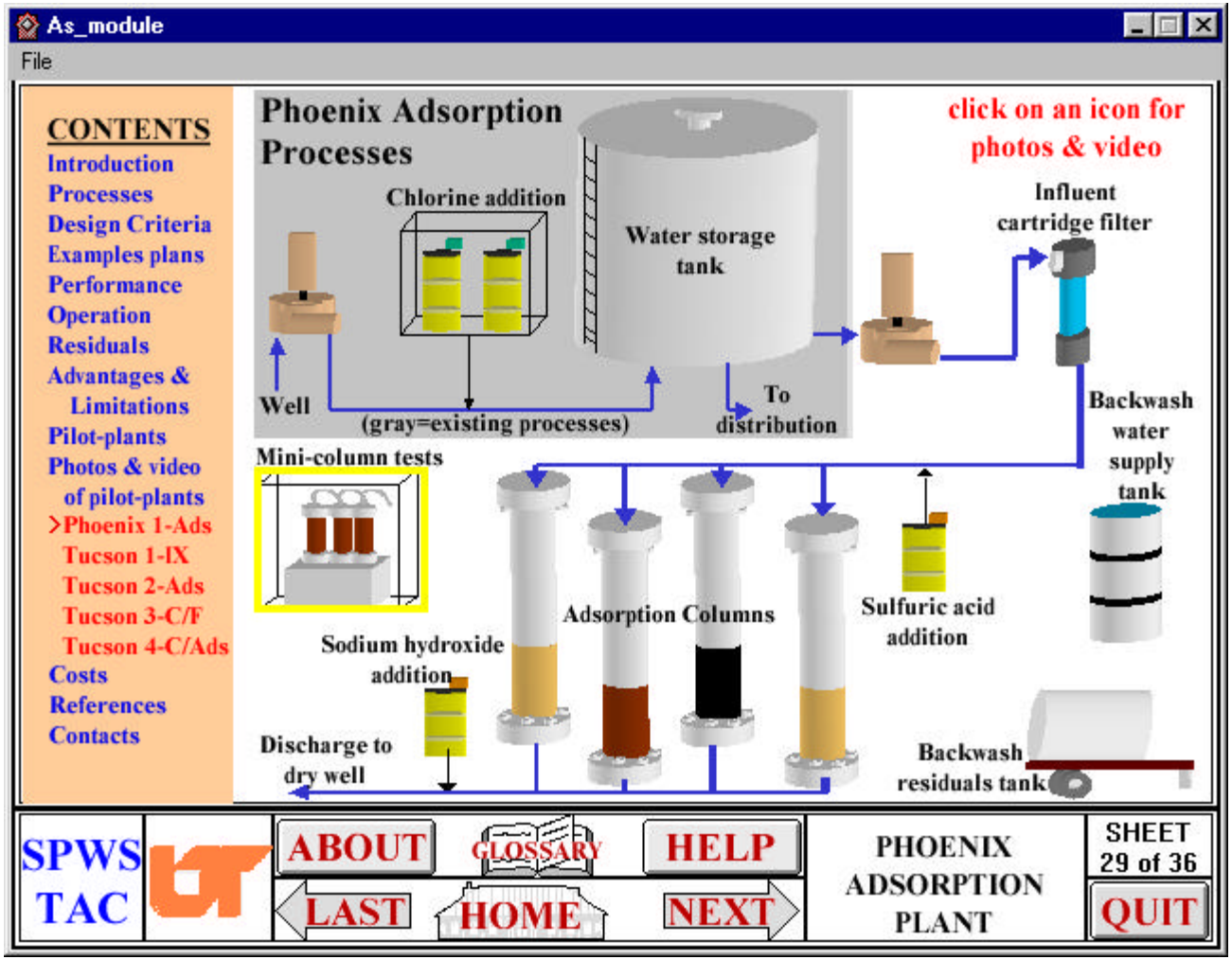
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Phoenix Adsorption Processes
Chlorine addition
Water storage tank
Well
(gray=existing processes)
To distribution
click on an icon for photos & video
Influent cartridge filter
Backwash water supply tank
Mini-column tests
Adsorption Columns
Sulfuric acid addition
Sodium hydroxide addition
Discharge to dry well
Backwash residuals tank
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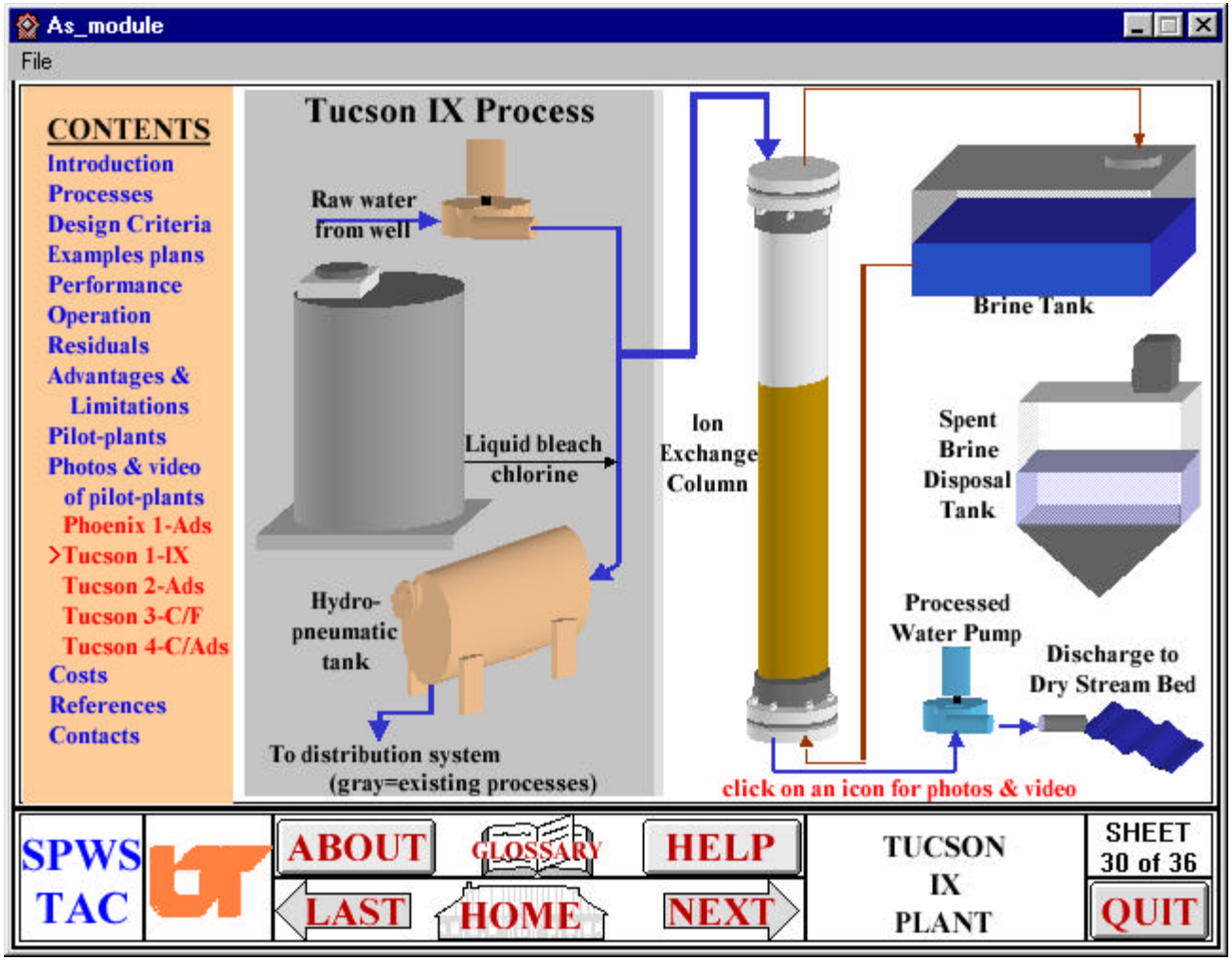
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Tucson IX Process
Raw water from well
Liquid bleach chlorine
Hydro-pneumatic tank
To distribution system
(gray=existing processes)
Ion Exchange Column
Brine Tank
Spent Brine Disposal Tank
Processed Water Pump
Discharge to Dry Stream Bed
click on an icon for photos & video
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TUCSON IX PLANT
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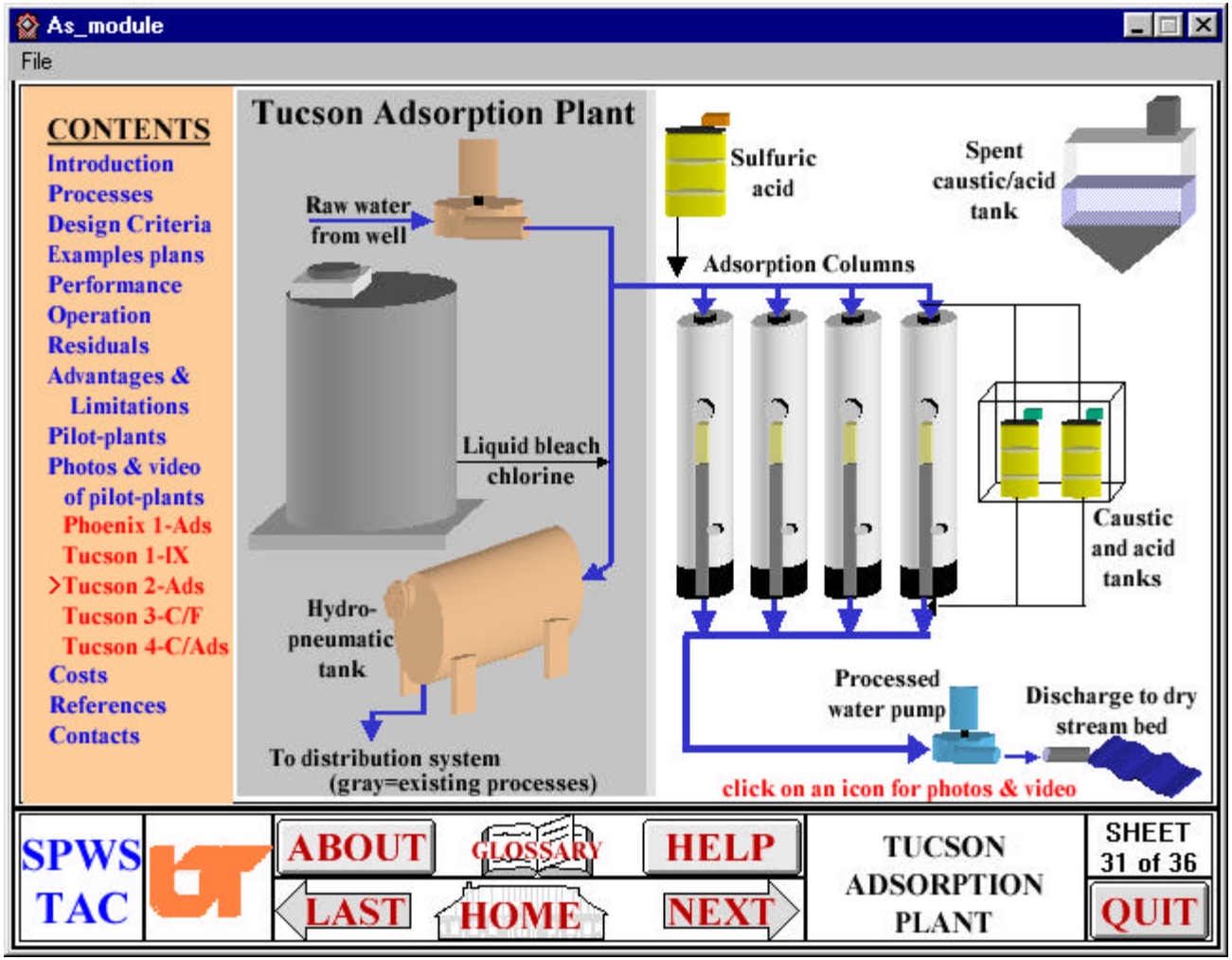
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Tucson Adsorption Plant
Raw water from well
Liquid bleach chlorine
Hydro-pneumatic tank
To distribution system (gray=existing processes)
Sulfuric acid
Spent caustic/acid tank
Adsorption Columns
Caustic and acid tanks
Processed water pump
Discharge to dry stream bed
click on an icon for photos & video
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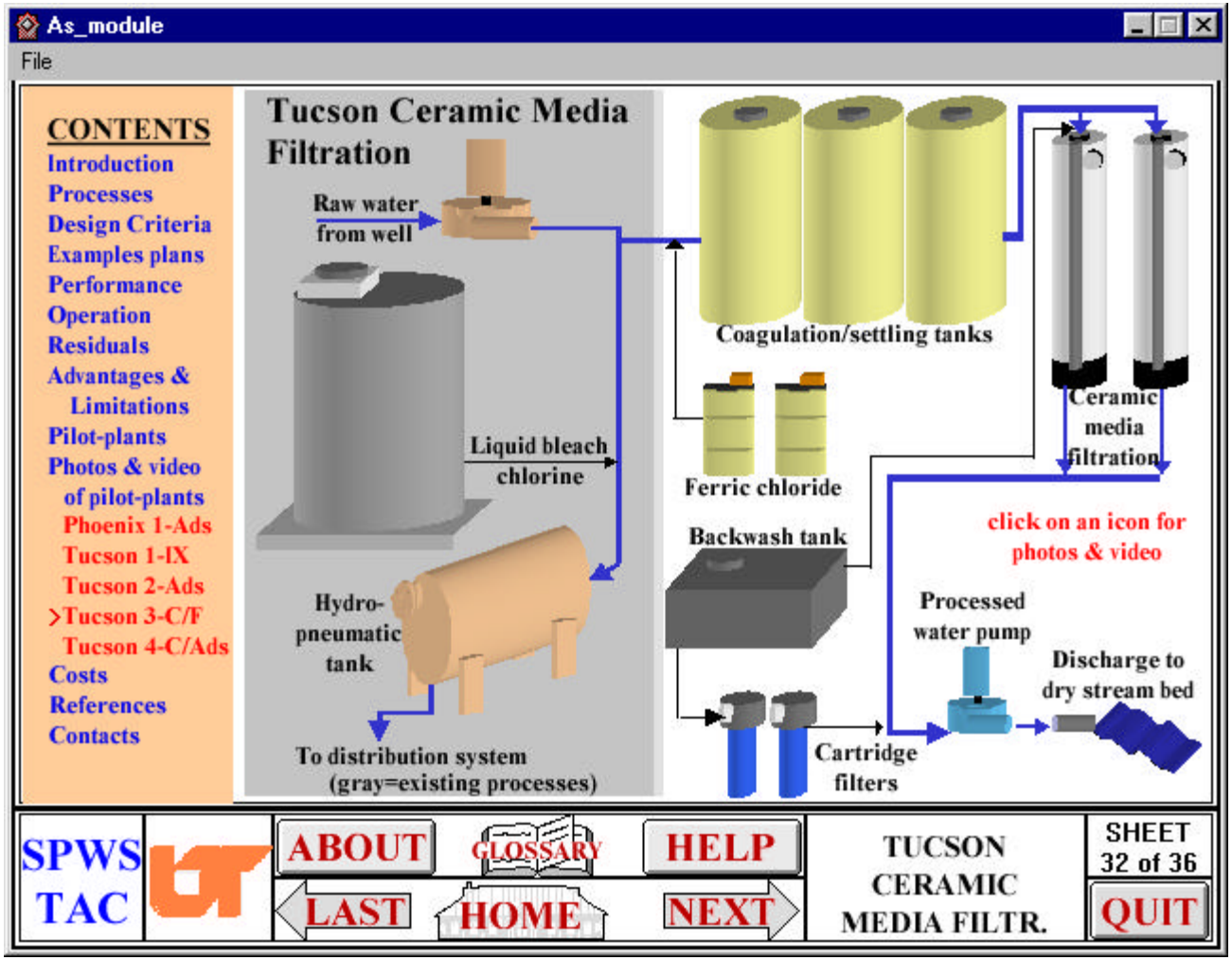
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Tucson Ceramic Media Filtration
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Ceramic media filtration
click on an icon for photos & video
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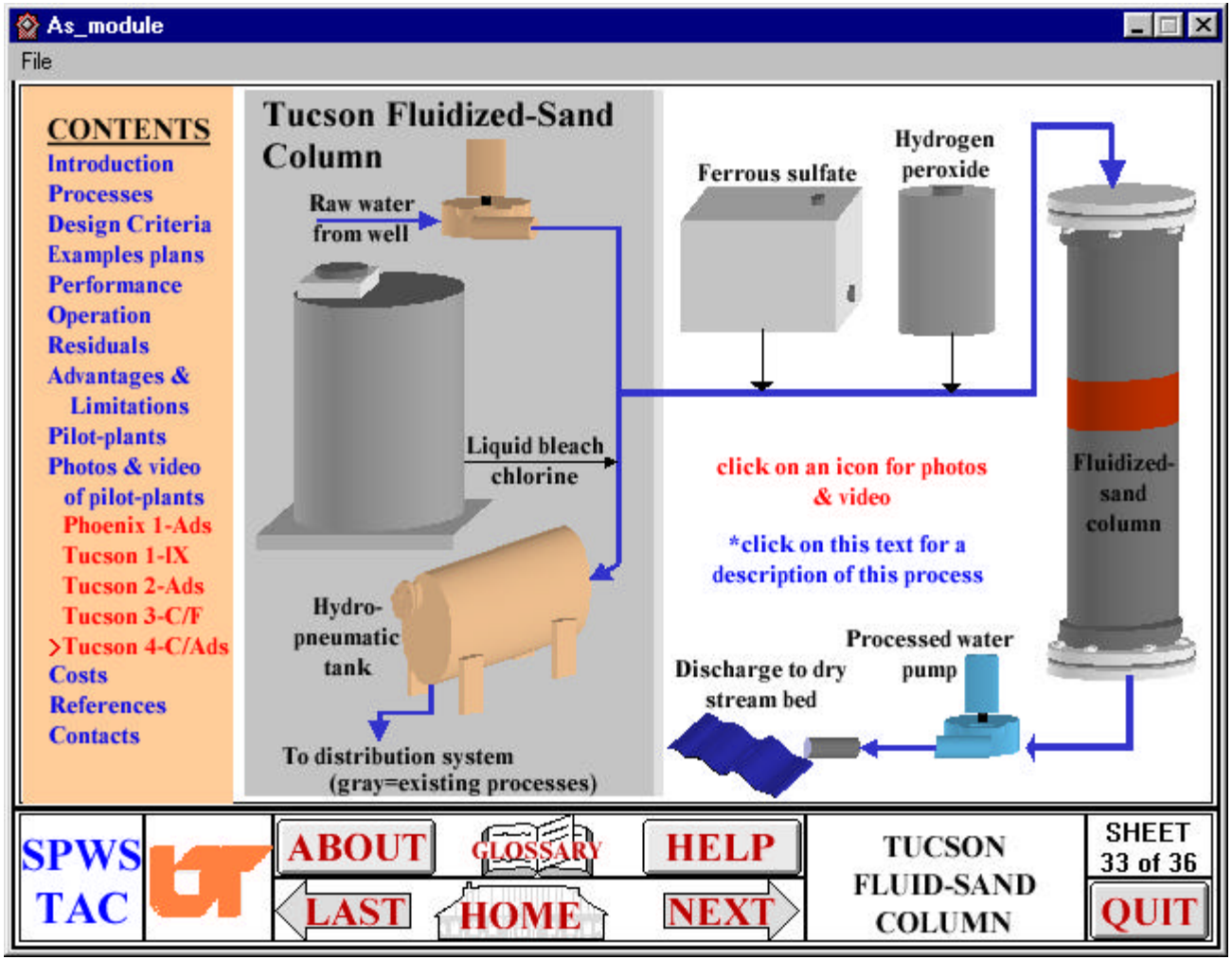
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Tucson Fluidized-Sand Column
Raw water from well
Liquid bleach chlorine
Hydro-pneumatic tank
To distribution system
(gray=existing processes)
Ferrous sulfate
Hydrogen peroxide
Fluidized-sand column
click on an icon for photos & video
*click on this text for a description of this process
Processed water pump
Discharge to dry stream bed
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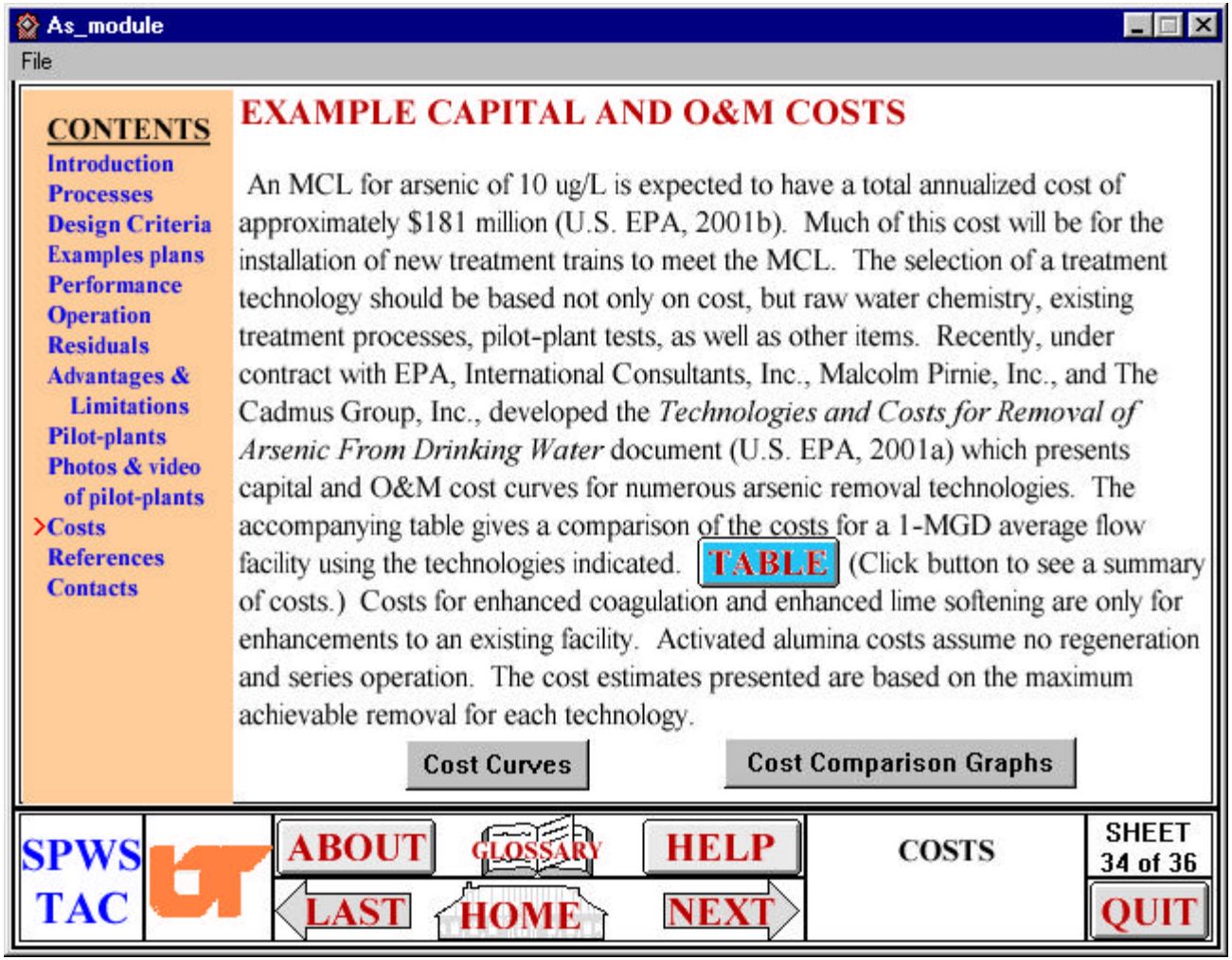
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EXAMPLE CAPITAL AND O&M COSTS
An MCL for arsenic of 10 ug/L is expected to have a total annualized cost of approximately $181 million (U.S. EPA, 2001b). Much of this cost will be for the installation of new treatment trains to meet the MCL. The selection of a treatment technology should be based not only on cost, but raw water chemistry, existing treatment processes, pilot-plant tests, as well as other items. Recently, under contract with EPA, International Consultants, Inc., Malcolm Pirnie, Inc., and The Cadmus Group, Inc., developed the Technologies and Costs for Removal of Arsenic From Drinking Water document (U.S. EPA, 2001a) which presents capital and O&M cost curves for numerous arsenic removal technologies. The accompanying table gives a comparison of the costs for a 1-MGD average flow facility using the technologies indicated. TABLE (Click button to see a summary of costs.) Costs for enhanced coagulation and enhanced lime softening are only for enhancements to an existing facility. Activated alumina costs assume no regeneration and series operation. The cost estimates presented are based on the maximum achievable removal for each technology.
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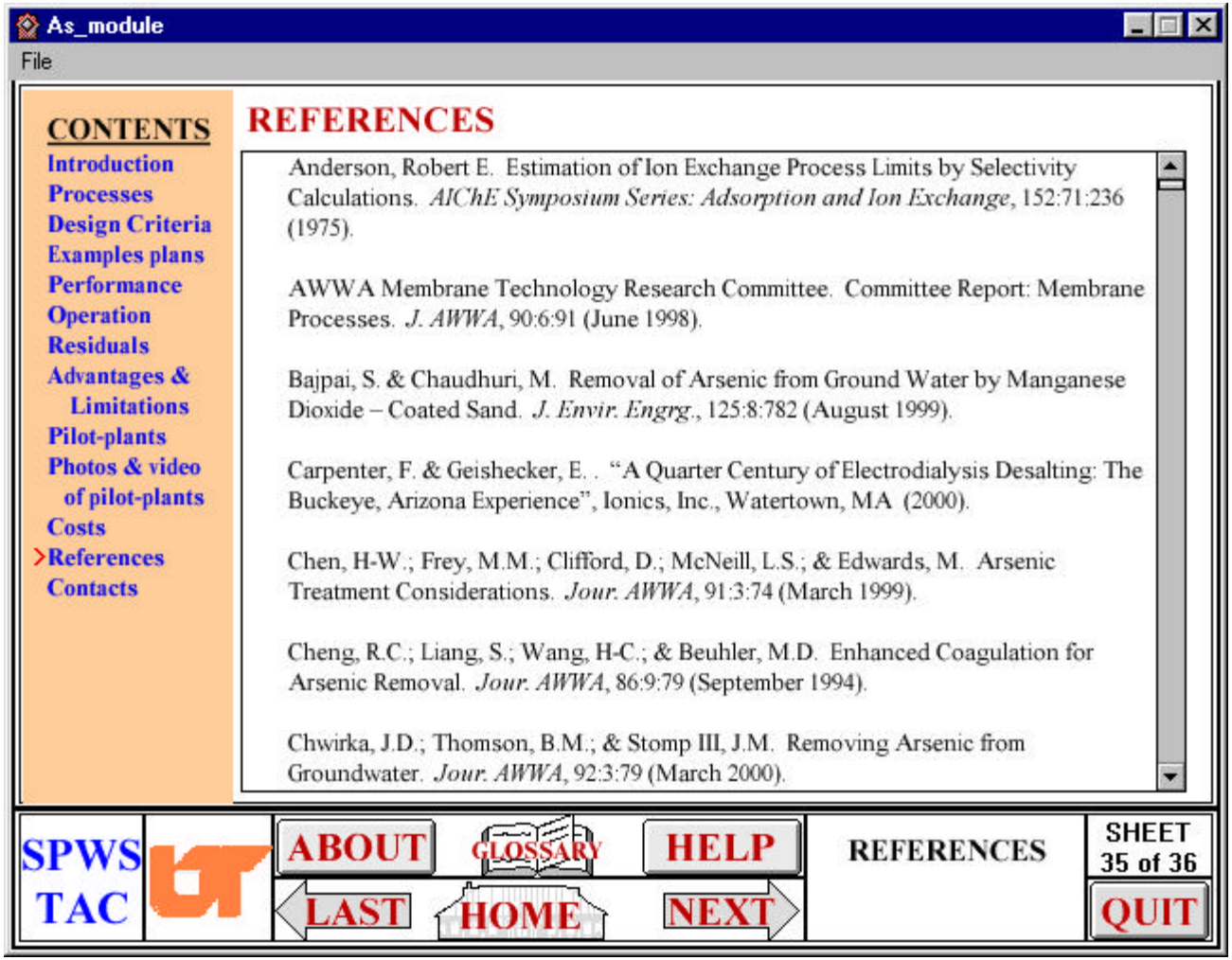
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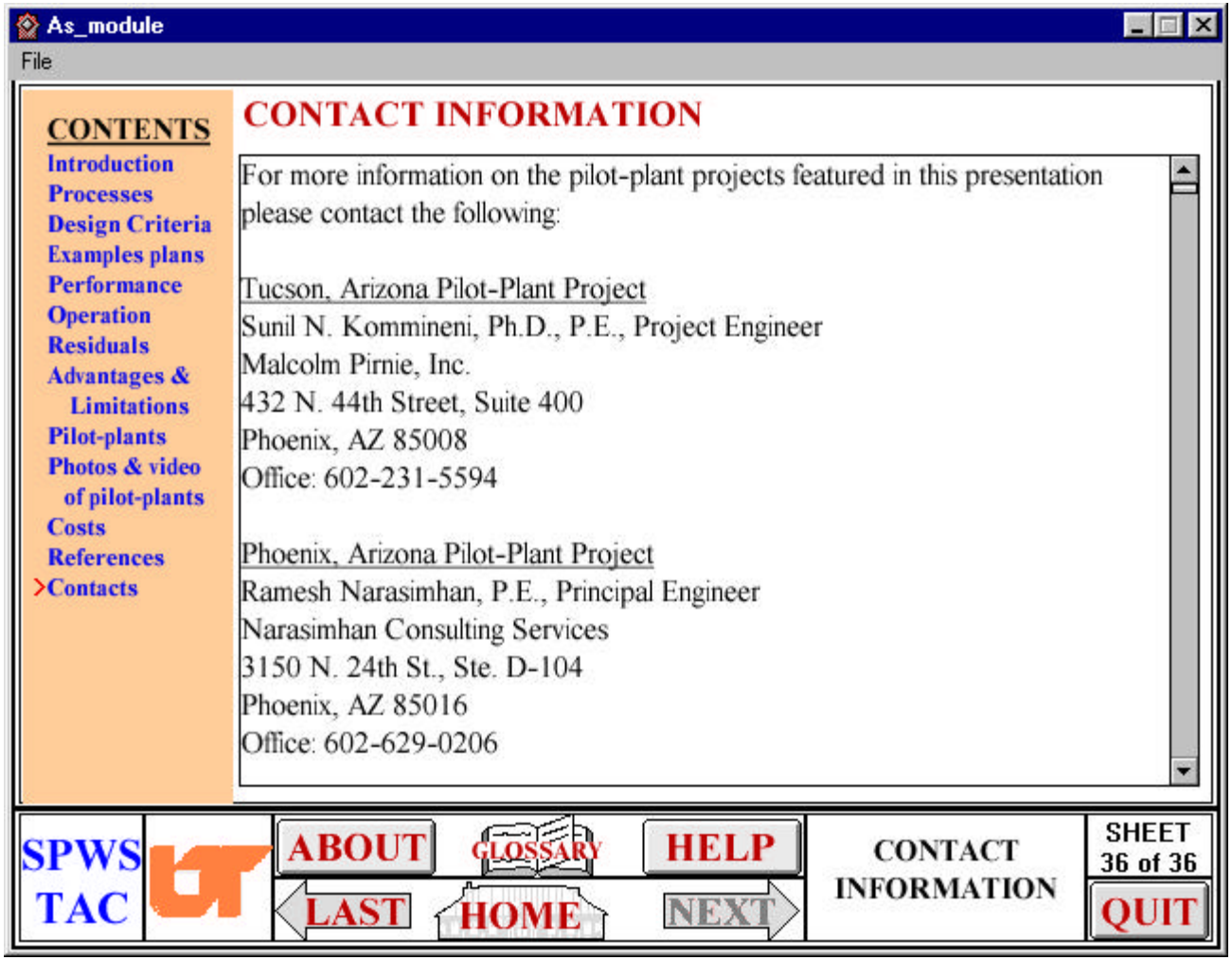
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VITA

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